DEMONSTRATION RESULTS
OF
HOT GAS DECONTAMINATION
FOR EXPLOSIVES

at

HAWTHORNE ARMY DEPOT

Hawthorne Nevada 89415-0015

VOLUME II OF IV

FINAL

Prepared for

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APPENDIX A

LABORATORY QUALITY ASSURANCE

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1.0 Introduction

The Analytical Laboratory of Support Services (ALSS), Tennessee Valley Authority, Resource Group located in Muscle Shoals, Alabama provided analytical chemistry support for a U. S. Army Environmental Center (USAEC) project concerning hot gas decontamination of explosives-contaminated munitions. The ALSS provided laboratory support in two major areas of the project:

1. Methods Development -- development of special sampling and analytical procedures that were required to fulfill the objectives of the project.

2. Sample Analysis -- analysis of routine samples generated during the HGD chamber tests at HWAAP.

This appendix provides a compilation of quality assurance activities ALSS provided in support of the HGD project.

2.0 General Information

2.1 Sample Turnaround Time

For the routine samples from the HGD chamber tests, ALSS was able to provide a satisfactory turnaround time for analytical data. Initial data reports usually consisted of spreadsheet printouts reviewed by the laboratory team leader. Complete data reports which were available after each run were interfaced with the Laboratory Information Management System (LIMS). Exhaustive data packages were made available at the end of the project. Quality control information for each run was available from

spreadsheet printouts. Detailed quality control summaries were available after data were interfaced with the LIMS.

2.2 Project Organization and Responsibilities

The laboratory team leader provided project oversight and was responsible for final data integrity. The laboratory team leader provided monthly ALSS project reports to USAEC, through TVA's project management staff.

During the course of the project, The Quality Assurance Officer of ALSS reported directly to the laboratory team leader and had no direct responsibilities in testing or analysis of the samples. The QA Officer was responsible for auditing actions and documentation to ensure adherence to this laboratory protocol. The QA Officer provided quarterly quality control data reports to the laboratory team leader.

Research Chemists and Analytical Chemists were responsible for planning, designing, testing, and documenting the various sub-projects assigned to them. They were responsible for producing periodic progress reports to the laboratory team leader. They were responsible for review of data falling under their areas of responsibility.

Chemical Laboratory Analysts were responsible for following procedures and instructions to provide analytical measurements required in the course of the project. They reviewed the data they produced, documented analytical runs, and performed equipment maintenance.

2.3 Research Records

Records from the project consist of data reports, bound research logbooks, instrument logs, worksheets, machine printouts, chromatograms, plots, and case narratives. Records will be accumulated with a copy sent to AEC (Environmental Technology Division) and a copy archived in a TVA record storage area.

Written procedures were produced in the course of this project. Procedures in final form were distributed to key staff members directly involved in the project. Copies will be archived in a TVA record storage area.

2.4 Sample Custody

All test samples from the HGD chamber tests were handled in accordance with ALSS procedure SP-0001, "Sample Chain of Custody." A few samples were broken in shipment and noted at the time of receipt at the laboratory. They were handled in accordance with SP-0001. A few others broken or cracked in shipment were found when containers were opened for analysis, but could be salvaged.

3.0 Analytical Procedures and Calibration

3.1 Methods Manual

Procedures used in this project were documented in a standard methods manual as described above. Procedures were:

HGD-0001 - "Spiking Explosives on Metal Surfaces"
HGD-0002 - "Extraction Experiments"
HGD-0003 - "Planning Sampling Activities and Sampling"
HGD-0004 - "Safety and Emergency Plans"
HGD-0005 - "Use of Explosives Storage Room"
HGD-0006 - "Method Detection Limits"
HGD-0007 - "EPA Wipe Sampling Technique"
HGD-0008 - "Ammonium Picrate Analysis by HPLC"
HGD-0009 - "Gas Phase Explosives Trapping Experiment:"
EPA Method 8330 "Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)" with Addendum

Procedure HGD-0002 was never distributed to the manuals in its final form. By its nature, it was being developed as the experiments were being

performed. The Addendum to EPA Method 8330 was utilized to clarify, interpret, and expand the procedure to apply to the sample types encountered in this project.

4.0 Data Reduction, Validation, and Reporting

4.1 Data Reduction

Analytical spectral data were calculated and reduced on vendor-supplied chromatographic software. For RDX and TNT analysis, this was the Varian LC Star Workstation Software. For picrate analysis, Beckman System Gold software was used. Additional spreadsheets were utilized to apply weight and dilution factors to this data and to calculate percent recovery on quality control samples. Further formatting software was utilized to place data in a form suitable for automatic interface to the LIMS. Procedure GLP-0017, "Control of Changes to Software" was utilized to document spreadsheets and programs utilized in final calculations and data interfacing. At times, analysts used the Star Workstation software or Beckman System Gold software to perform manual baseline fits, depending on the nature of the chromatograms. This was documented in run narratives or noted on machine printouts.

4.2 Data Validation

Analytical measurements were first reviewed by the chemist producing them and then passed either to the team leader or group leader for further review. After approval, data were interfaced with the LIMS system which performs automatic calculation of percent recovery for spiked samples and control samples. The LIMS software was capable of flagging spikes, blanks, and control samples which fell outside predetermined limits. The spreadsheet used for RDX and TNT final calculations also flagged samples which fell above the high end of the calibration curve. Such samples were either accepted on a "use as is" basis or reanalyzed at the discretion of the Team Leader.

4.3 Data Reporting

As mentioned above, data were reported initially from spreadsheets to the team leader who passed the information as rapidly as possible to the field engineers. Following this, analytical runs were interfaced with the LIMS and a formal report was made available.

All analytical data from a single HGD chamber test were accumulated and stored as an analytical data package. Each package included as a minimum:

- Sample description or identification information.
- Sample analytical results.
- Quality control sample results with percent recovery of the added compounds.

4.4 Records Retention

Records of experiments and analyses will be maintained for a period of three years after the end of the project in a TVA record storage area. This will include machine printouts or chromatogram traces, logbooks, notebooks, log-sheets, standard material use logs, raw data calculation sheets and the like. Records will be stored for experiments, analytical measurements, and determination of Method Detection Limits (MDLs). Computer media utilized to store analytical file backups or raw data files will be stored for the lifetime of the project plus one year (through December 1995) due to the limited lifetime of computer storage media.

Data from failed attempts at analysis will be maintained along with supporting documentation.

4.5 Data Qualification Codes

Abbreviation codes which may appear in the analytical data packages include:

NA - Compound Not Analyzed

<MDL or ND - Compound not detected (analysis value falls below the method detection limit (MDL))

TR or Trace - Compound present at trace level (i.e., there was an indication of the compound, but the concentration was less than the MDL and was too low to quantify.)

5.0 Internal Quality Control Checks

5.1 Setup QC

5.1.1 General

ALSS demonstrated that glassware and reagents were free of interferences by running blank samples. Blanks included acetonitrile, water, methanol, or any other solvents used in the various process. Blanks included extracts of clean smears.

Initially, ALSS ran QC check sample sets of known concentration to ensure method precision and accuracy were well defined.

Retention time windows for laboratory analysis equipment were established in order for software to function properly.

Each analyst demonstrated the ability to generate acceptable results with the methods before beginning work on project samples.

Finally, three sets of samples containing TNT and RDX were prepared at TVA. One set was shipped to CRREL. One set was packaged as for shipment and stored on a bench top at TVA. This set was prepared so that a set would be analyzed at TVA which matched temperature conditions of the set shipped to CRREL. A portion of the third set was analyzed on the day the three sets were prepared (to verify that

preparation of the samples was correct) with the remainder being refrigerated at TVA until CRREL received their shipment. On the same day CRREL received and analyzed the set shipped to them, the refrigerated set and packaged set were analyzed by TVA. In this way the three sets of samples could be compared to each other. All measurements made on all three sample sets at both laboratories were consistent.

5.1.2 Method Detection Limits

ALSS determined method detection limits as defined in 40 CFR Part 136, Appendix B, Revision 1.11. Detection limits were documented in internal memoranda with associated data packages. Detection limits for HPLC analyses were found to be a function of column age, and detector stability.

The method detection limit for picrate was determined to be 0.004 micrograms per milliliter (ppm) for extract solutions. Due to a misunderstanding of how to interpret 40 CFR Part 136, it was initially thought to be 0.017 ppm. However, once the misunderstanding was resolved, all data reported with the higher detection limit were reassessed and corrected.

The various detection limits found for RDX and TNT are tabulated here. Values are reported as micrograms per smear and as micrograms per milliliter of extract.

	RDX	TNT
	µg/smear (µg/mL)	µg/smear (µg/mL)
June 3, 1994	0.7 (0.007)	0.3 (0.003)
July 29, 1994	0.7 (0.007)	0.4 (0.003)
August 24, 1994	0.4 (0.004)	0.25(0.0025)
September 23, 1994	1.0 (0.010)	0.6 (0.006)

5.1.3 Retention Time Windows

Retention time windows were determined by making three injections of each analyte during a 72-hour period. Retention times were determined for each of these injections. The means and standard deviations of the retention time data were calculated. Limits were calculated at plus or minus three standard deviations from the mean. The automatic peak-identification software could only accept one window width for its calculations; so for RDX and TNT, an average window value was used. When a new column was installed, retention time windows were reassessed against peaks observed in quality control samples to ensure they were still adequate.

5.1.4 Method Accuracy and Precision

Quality control check samples, produced independently from the calibration standards and which contained each analyte of interest, were utilized to track method accuracy and precision. The recovery was calculated for each analyte and reported to the team leader for review with each data set. These were termed "laboratory control samples" and are discussed below.

5.2 Calibration QC

5.2.1 Method 8000A/8330 Calibration QC

Calibration was performed in triplicate with standards of five concentrations over the range of linear response of the device. The lowest concentration was approximately equal to the method detection limit. Calibration standards were loaded in random order. Calibrations were performed before analysis of samples and at any time thereafter when quality control samples indicated the calibration factors had changed.

In the early parts of the project, linear regression fits were made with lines forced through the origin and again with lines not forced through the origin (viz. to equations of the form $y=mx$ and of the form $y=mx+b$).

Comparisons were made of the residual sum of squares and the magnitude of the intercept to determine whether the points fell in the linear response range of the device. The curve with the best residual sum of squares was utilized. Shortly after the beginning of the project, policy was changed so that only curves of the form $y=mx$ were used.

At the beginning of each run, the midpoint calibration standard was analyzed in triplicate. The response factor for the average of these three points had to be within 15 percent of the response factor for the initial calibration (That is, the percent recovery must fall between 85 and 115 percent.) If not, the machine was recalibrated. Following this, at least every ten samples and at the end of the run a single midpoint calibration standard was run. The response factors for these had to fall within 15 percent of the mean daily initial response factor or all samples between the last valid calibration check and the next valid check were reanalyzed. These samples may also be called "initial calibration verification" and "continuing calibration check" samples.

Exception: At the team leader's discretion, if samples could be determined to contain none of the analyte of interest by automatic peak search and by visual inspection of the chromatograms, the samples were not reanalyzed

Results of the midpoint calibration standards are plotted in Figures A-1, A-2, and A-3 for RDX, TNT, and picrate, respectively. Values plotted are the percent recovery for the measured values. The X-axis of the plot is the sequence number of the quality control samples for the course of the project. Percent recovery is calculated by the following formula:

$$\% \text{ Recovery} = 100 * (\text{Measured Value} / \text{Known Value})$$

A slight downward trend can be detected in the latter half of the RDX data. Only a few points fall out of control. TNT data appear to be

separable into two groups with separate mean values. Latter values tend to fall below the lower control limit more frequently than RDX. Early on, one value each for RDX and TNT was unexpectedly high. By comparison, picrate analyses appear very stable. The downward trends here for RDX and TNT and in other quality control data discussed below are perhaps indicative of column deterioration or slow degradation of the detector over the course of the latter half of the project. The very last few points on the RDX and TNT plots are associated with test runs 33 and 34. During analysis of these samples, a very broad peak with a long retention time was noted. The retention time was so long that it would often appear in later samples, interfering with peaks for RDX and TNT. These samples were run multiple times and in various orders in an attempt to obtain good data. In some runs, only one or two samples were acceptable. It should be noted that several runs for these two tests are reflected in the quality control data reported here, some with recoveries which were judged unacceptable upon initial review. The data from test runs 33 and 34 were qualified as "not quantifiable."

A daily retention time window was calculated for each analyte using the mean retention time from the initial midpoint calibration standard plus or minus three standard deviations, as determined in the set-up QC section. If the retention time for any analyte from subsequent midpoint calibration standards fell outside the window, those samples analyzed between two valid midpoint calibration standards were flagged and passed to the team leader for review. At his discretion they were reanalyzed. In this case, the software would not identify the peaks as the analyte of interest and they were identified by visual inspection of the chromatograms.

5.3 Batch QC

5.3.1 Definitions

Batch - A group of no more than 20 samples of the same matrix prepared or extracted at the same time with the same reagents.

Note: When ALSS began the project, solvent samples, smear extracts, and solutions of solid materials were counted as different matrices. In this way each matrix would be considered part of a separate batch. After gaining some experience with the sample types, it was determined that smear extracts and solutions behaved in a similar manner and were considered as the same matrix for determining batch sizes.

Method Blank - A sample of clean reagent carried through preparation and extraction in the same manner as samples.

Matrix Spike - An aliquot of a sample spiked with a known concentration of all target analytes. Spike concentration was usually chosen to read at the midpoint of the calibration curve.

Matrix Spike Duplicate - A second aliquot of the same sample treated as the matrix spike.

Quality Control Check Sample - A sample containing mid-range concentrations of analytes of interest with concentrations known to the analyst. This sample is made from a separate stock of standard material than calibration solutions when possible. This sample type may also be referred to as a "laboratory control sample."

Duplicate - A second aliquot of a sample.

5.3.2 Batch QC Samples

One quality control check sample (laboratory control sample) was run with each batch. These are plotted in Figures A-4, A-5, and A-6. Percent recovery was calculated as for midpoint calibration standards. Again percent recovery is plotted as a function of sample sequence. RDX data show a downward trend over the course of the project. TNT data, by

comparison, are relatively stable but tend to have a few points with unexplained low recoveries. Picrate results are very stable.

One matrix spike and one matrix spike duplicate were run with each batch. Plots of percent recoveries for these samples are appended as Figures A-7, A-8, and A-9.

For matrix spikes, the percent recovery is calculated as follows:

$$\% \text{ Recovery} = 100 * (\text{FOUND} - \text{UNSPIKED})/\text{SPIKE}$$

Where

FOUND is the concentration measured for the spiked sample
UNSPIKED is the concentration measured in the unspiked sample
SPIKE is the amount added to the matrix spike sample in concentration units

RDX shows an upward trend followed by a downward trend. TNT data held steady in the first half of the project and then show a downward trend. However, the extreme downturn for the very last matrix spike sample recovery is a reflection of difficulty in measurement for samples from tests 33 and 34. The broad, unidentified peak with a long retention time was present as discussed above. This peak interfered with analysis of RDX and TNT. These samples were run multiple times in an attempt to obtain good data. In some runs, only one or two samples were acceptable. It should be noted that several runs for these two tests are reflected in the quality control data reported here, some with unacceptable recoveries. The data from test runs 33 and 34 were qualified as "not quantifiable."

Plots of relative percent differences between matrix spikes and matrix spike duplicates are appended as Figures A-10, A-11, and A-12. Values

are good for all three analytes. Relative percent difference is calculated by the following formula:

Relative percent difference = 100 *(REC1 - REC 2)/[(REC1 + REC2)/2]

Where

REC1 is the percent recovery of the matrix spike sample
REC2 is the percent recovery of the matrix spike duplicate sample.

One method blank was run with each batch. Additional reagent blanks were run regularly. Of the 283 method and reagent blanks run with Method 8330, six of them had RDX above the detection limit and ten of them had TNT above the detection limit. Each of these was individually inspected. Of twelve reagent and method blanks for picrate analysis, no values were encountered above the detection limit.

Whenever the sampling organization in the field submitted additional samples as quality control checks these were counted as routine samples in determining batch size for the other quality control sample types. These were termed "field QC samples." A high concentration field QC sample and a low concentration field QC sample were included at the sampling location along with each set of 20 samples for every test run. The low concentration sample was one tenth the concentration of the high concentration sample. Since standard reference material was not utilized in making the field QC samples, the field sampling team always included a sample of the original stock solution which was used in making the field QC samples. The value from analysis of the stock solution was used as the known value in determining percent recovery. Plots of recoveries for high field QC samples are attached as Figures A-13, A-14, and A-15. Percent recovery was calculated as for midpoint calibration standards.

RDX and TNT both had fairly good recoveries with a pair of low values observed in the latter half of the project. Picrate analyses were good. Plots of recoveries for low field QC samples are attached as Figures A-16, A-17, and A-18. The low field QC samples showed greater scatter than the high QC samples. Both RDX and TNT had a high bias and occasional unexplained high recoveries for these samples. Picrate analyses were fairly good with one poor recovery.

6.0 Performance and System Audits

The ALSS Quality Assurance Officer introduced blind quality control samples using recovered flake material. Recovered values are appended as Table A-I. Recoveries were calculated using literature values as percentages of RDX and TNT in HBX and COMP-B recovered flake. It appears that the material labeled as HBX did not contain the expected quantity of RDX.

Table A-1
Blind Quality Control Samples from Reclaimed Material

Date	Analysis for	Found mg/l	Known mg/l	% Recovery *
5/6/94	TNT	57.7	52.5	109.9
5/6/94	TNT	53.7	52.5	102.3
7/20/94	COMP-B TNT	6.3	6.3	100.0
	COMP-B RDX	8.4	9.5	88.6
9/21/94	HBX - RDX	9.9	10.4	95.7
	HBX - TNT	14.4	9.8	146.8
9/21/94	COMP-B RDX	16.6	18.5	89.7
	COMP-B TNT	12.4	12.4	100.1

* Recovered flake material may not have RDX and TNT present in ratios stated in the literature. Percent recovery is calculated based on literature values.

The ALSS Quality Assurance Officer inspected control charts, logs, records, printouts, results of quality control checks, documentation, case

narratives, research notebooks, and other quality related aspects of the project to ensure detailed compliance was in effect. Results of one review were reported in writing to the Laboratory team leader as an internal audit. In that audit, it was noted that one type of quality control check samples had been omitted in designing runs for Method 8330. Since corrective action was immediate, no nonconformance report was issued. Other minor areas of concern were identified and reported in quarterly reports to the manager.

7.0 Calculation of Data Quality Indicators

7.1 Common Data Quality Indicators

Relative percent difference, standard deviation, accuracy, and other commonly used statistical indicators were calculated as defined in Chapter 1 of SW-846, 3rd Edition utilizing the LIMS software. Since analytical work went so rapidly, completeness was not found to be a useful indicator and was not calculated or monitored.

Method Detection Limits were be calculated as defined in 40 CFR 136, Appendix B.

Method Quantitation Limits were defined as five times the Method Detection Limit as in 40 CFR 136, Appendix B.

8.0 Quality Control Reports to Management

Quarterly quality control data report were written by the ALSS QA Officer addressing:

- Changes in the laboratory's portion of the QA Project plan.
- Changes in analytical procedures.
- Summary of QC program results, summary of training, summary of accomplishments.

- Results of audits, results of performance sample evaluations, and any significant problems with problem resolutions.
- Data quality assessment in terms of precision, accuracy, and MDL.
- Discussion of whether QA objectives were met.

These reports were included with routine internal quarterly quality control reports.

9.0 Overall Assessment of Data Quality

The data presented here provide a picture of a complete, operational quality control program. The quality control measures which were applied met their intended purposed. That is, they provided timely identification of problems during the course of the project so that the they could be resolved wherever possible. Outliers were investigated and corrections were made. The vast majority of the data fell within the 85 to 115 percent window (or 75 to 125 percent window for matrix spikes) allowed under EPA protocols. However, corrective measures were often attempted well before data fell outside control limits. It must be emphasized that outliers were individually investigated and assessed by the laboratory. The fact that outliers are reported here does not invalidate the entire data set, but instead gives a complete picture of the dynamics of the measurement process encountered by any working laboratory.

These quality control activities, demonstrate that the analytical techniques were sufficiently accurate, precise, and sensitive to meet the needs of this project for data quality. When coupled with the other parts of the overall quality assurance program, the quality control data provide significant assurance that the samples were handled, stored, prepared, and analyzed in a documented and reproducible manner.

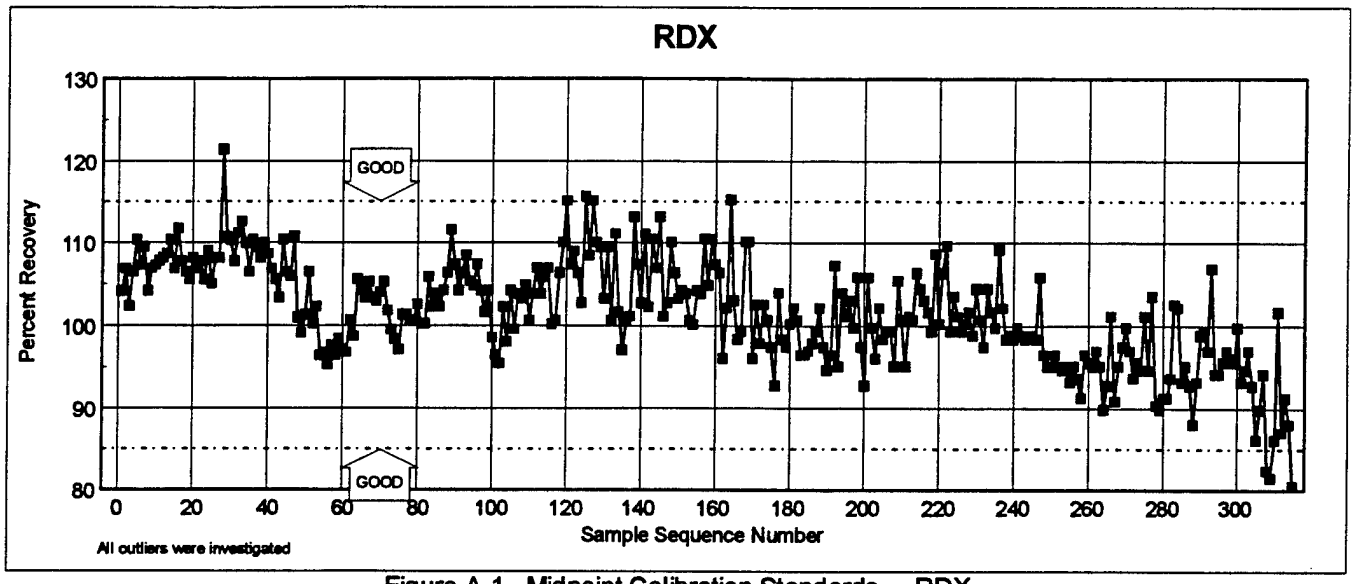

Figure A-1 Midpoint Calibration Standards - RDX

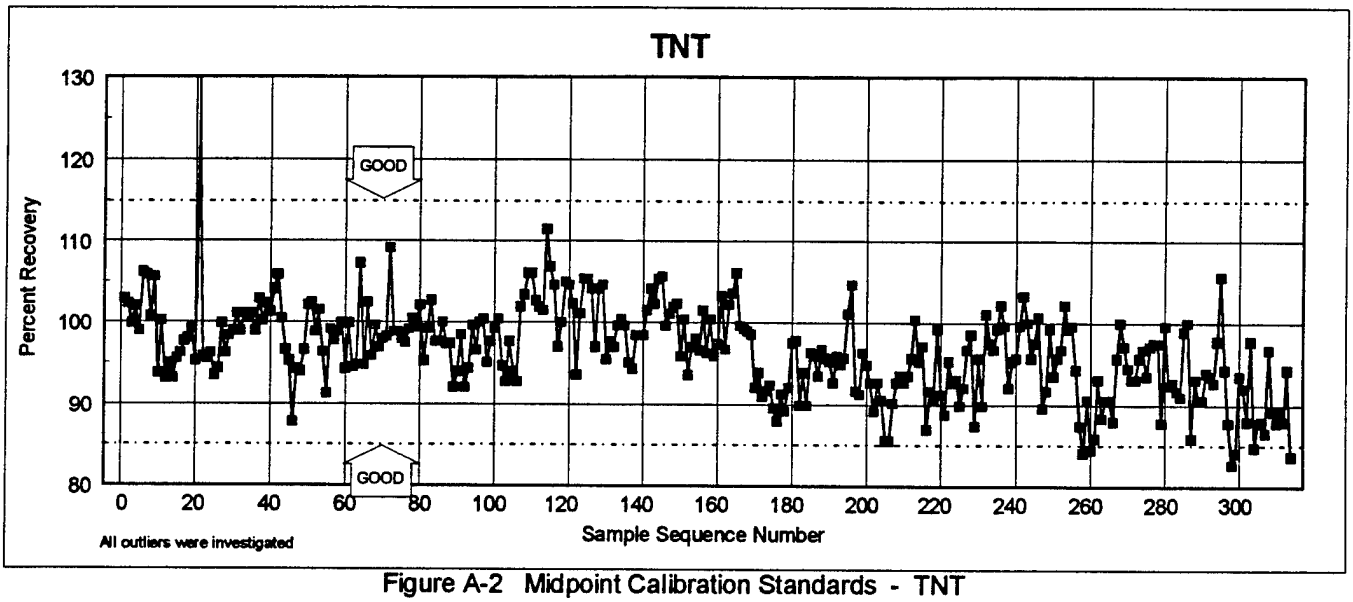

Figure A-2 Midpoint Calibration Standards - TNT

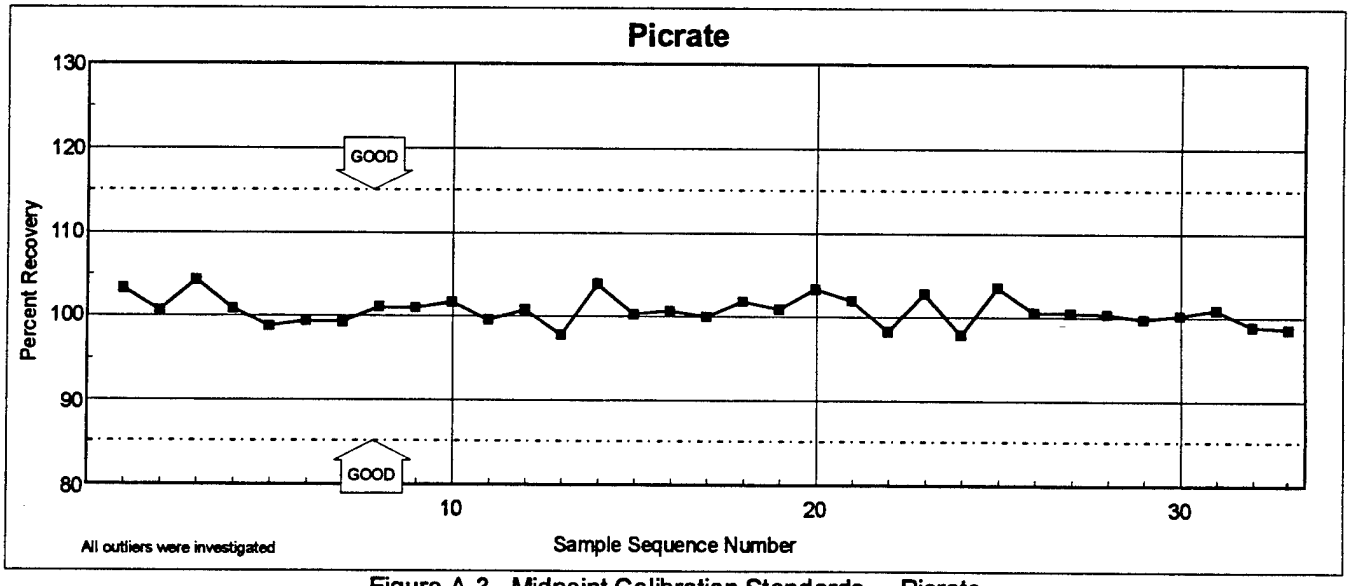

Figure A-3 Midpoint Calibration Standards - Picrate

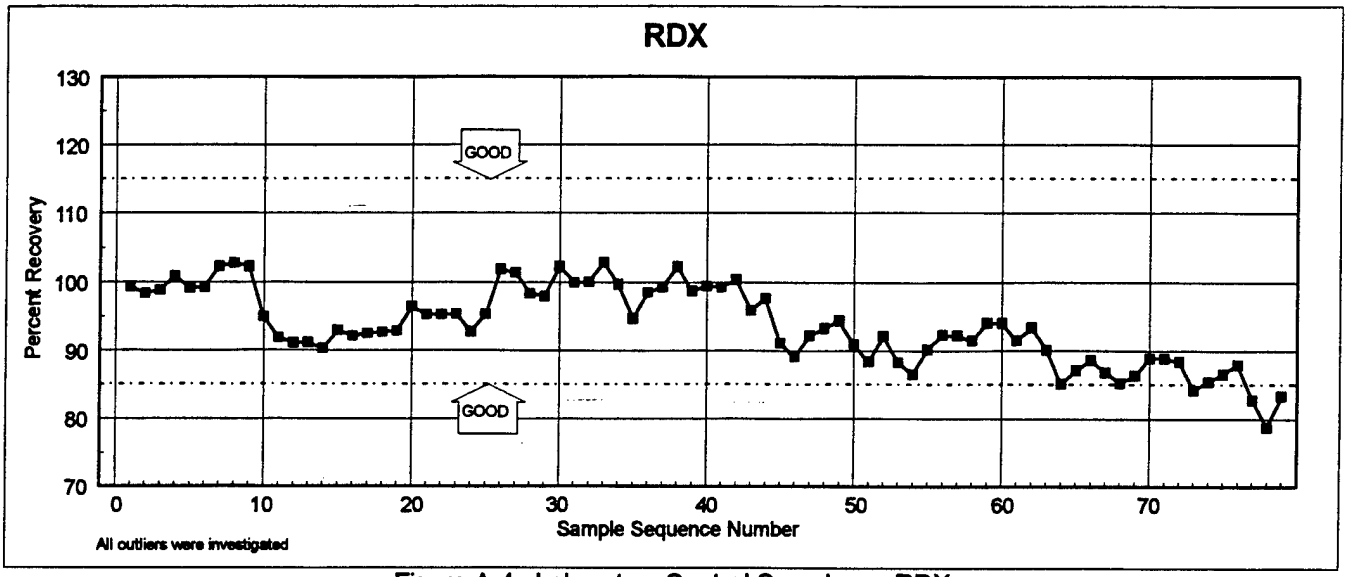

Figure A-4 Laboratory Control Samples - RDX

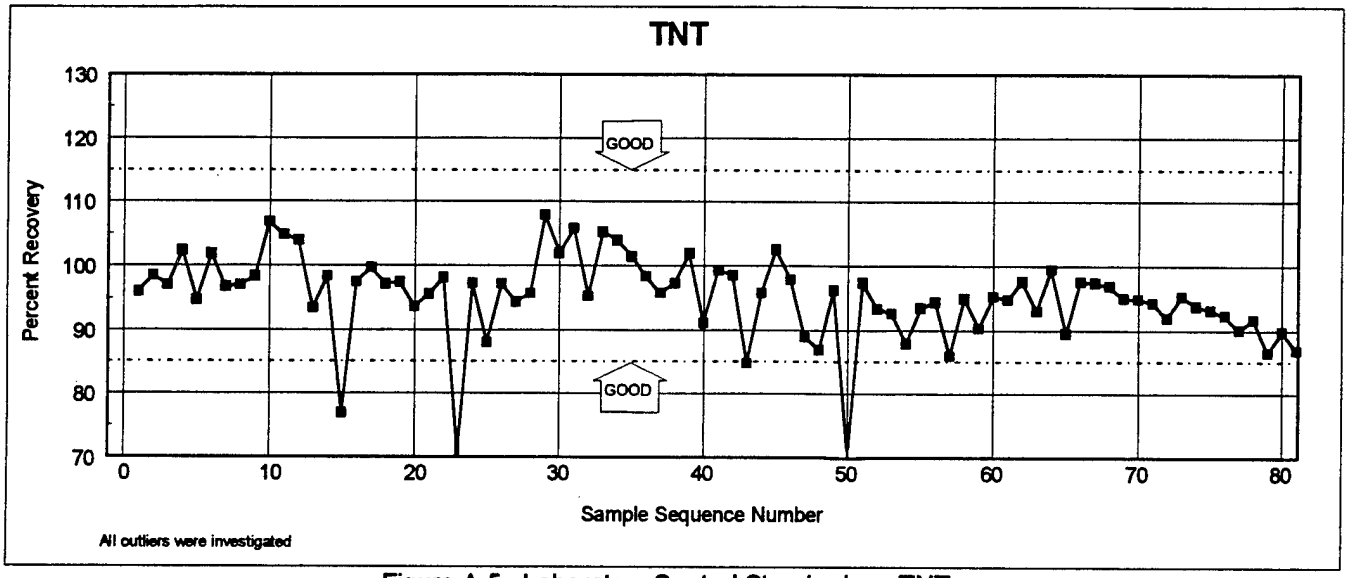

Figure A-5 Laboratory Control Standards - TNT

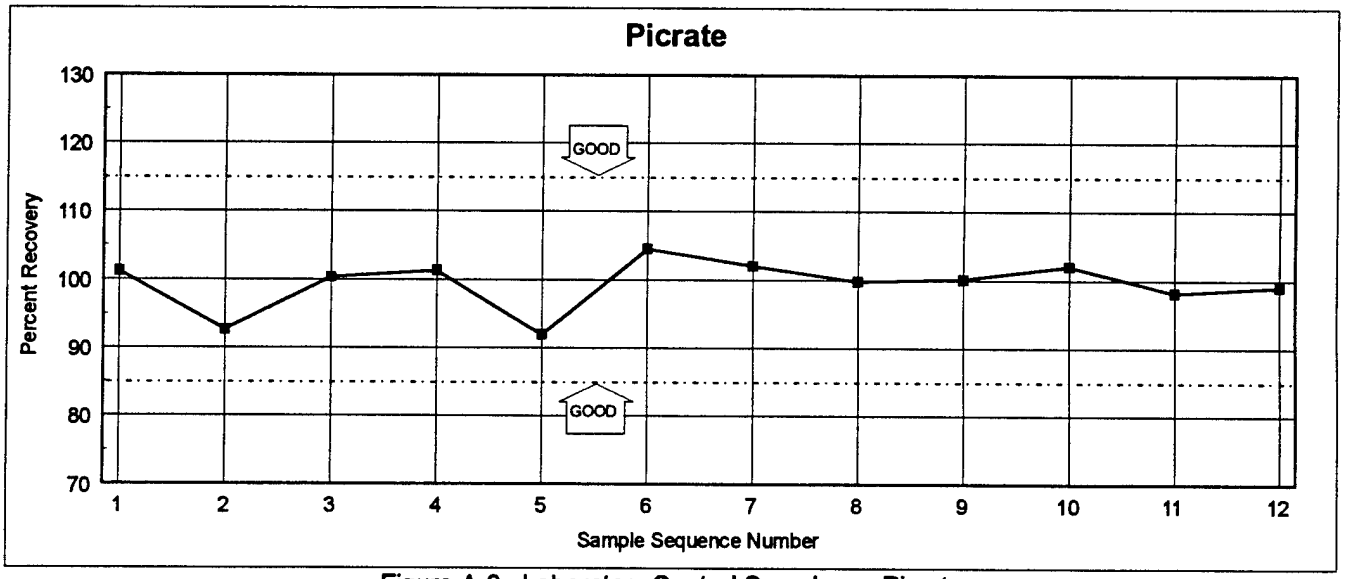

Figure A-6 Laboratory Control Samples - Picrate

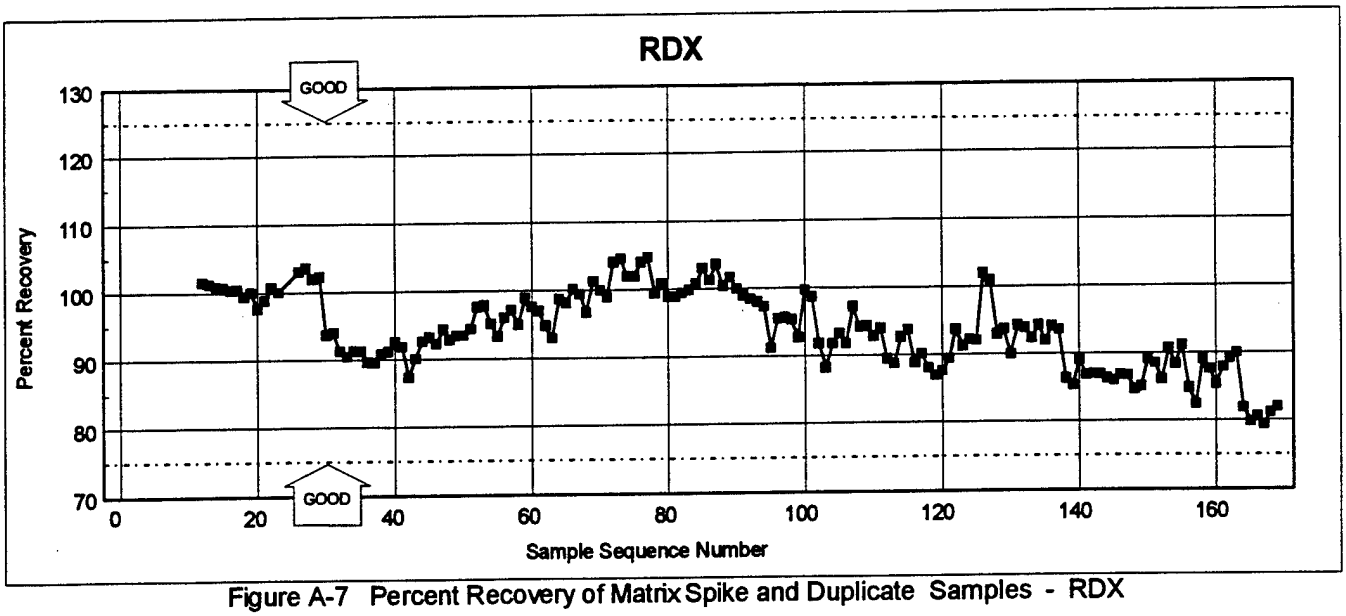

Figure A-7 Percent Recovery of Matrix Spike and Duplicate Samples - RDX

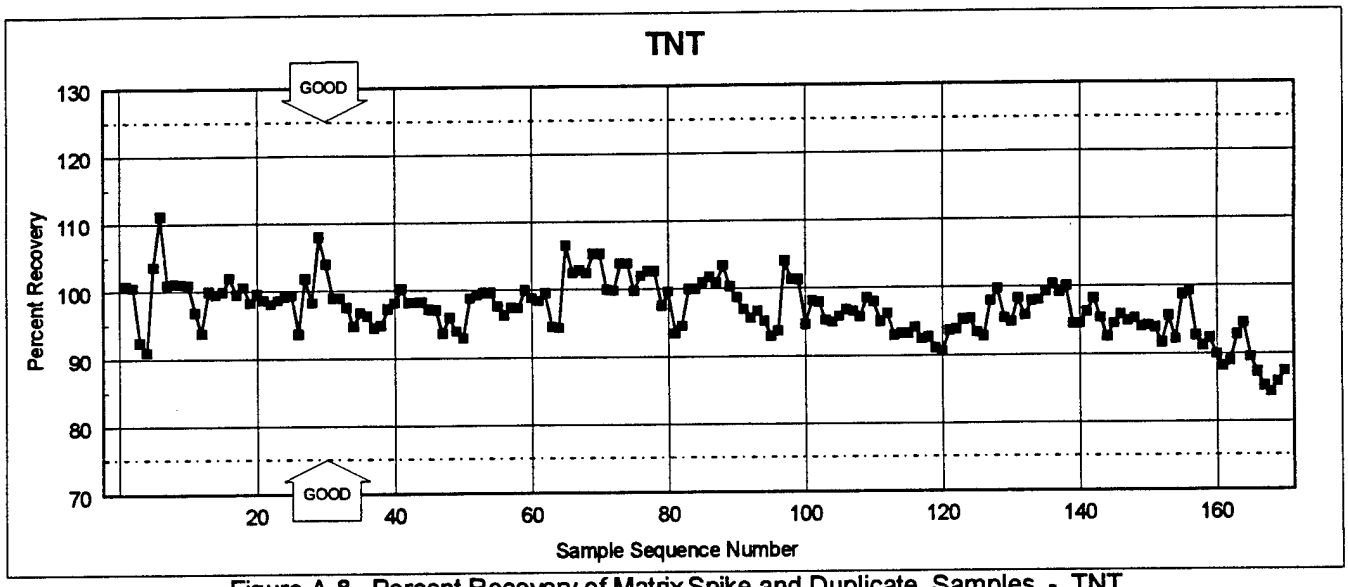

Figure A-8 Percent Recovery of Matrix Spike and Duplicate Samples - TNT

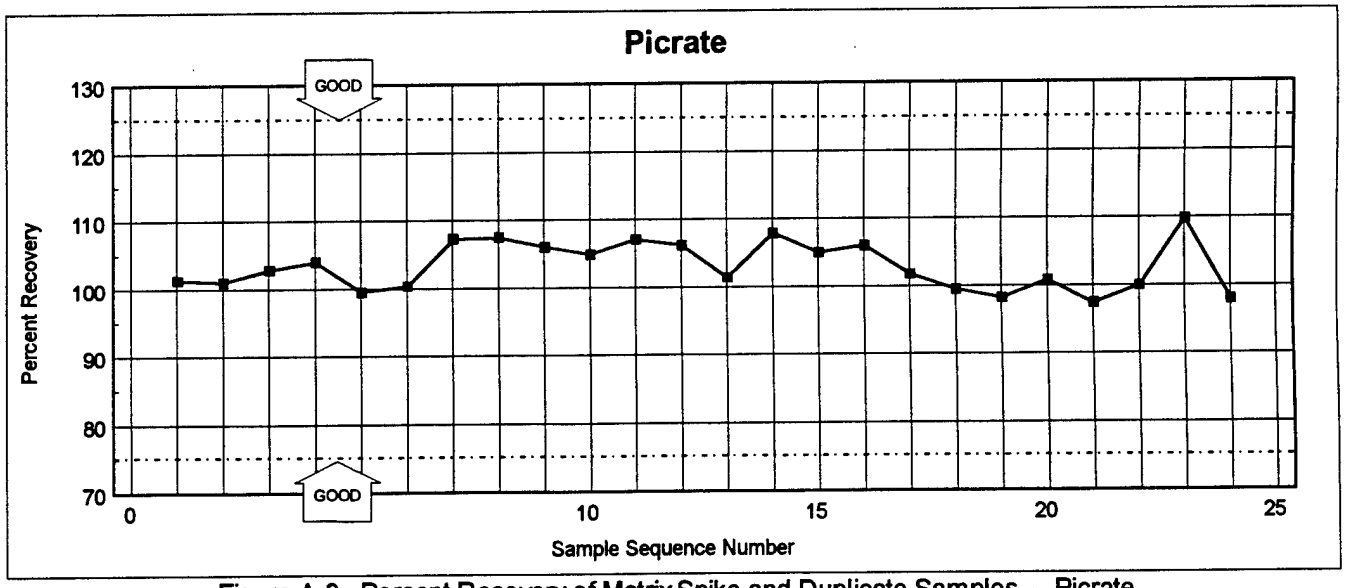

Figure A-9 Percent Recovery of Matrix Spike and Duplicate Samples - Picrate

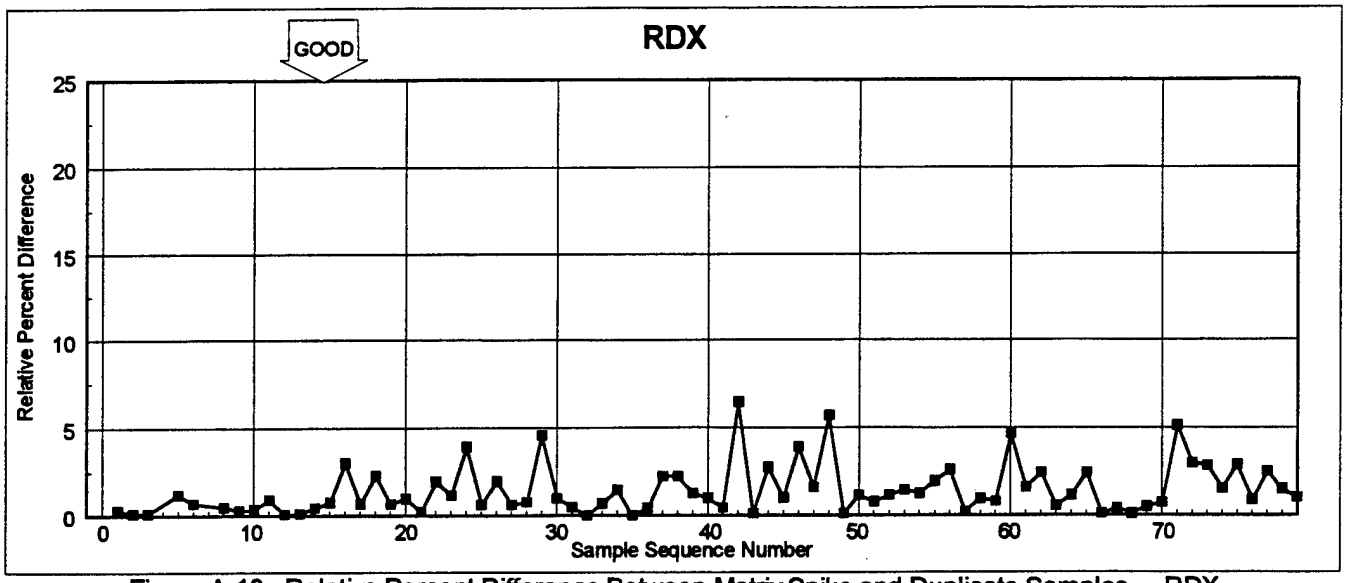

Figure A-10 Relative Percent Difference Between Matrix Spike and Duplicate Samples - RDX

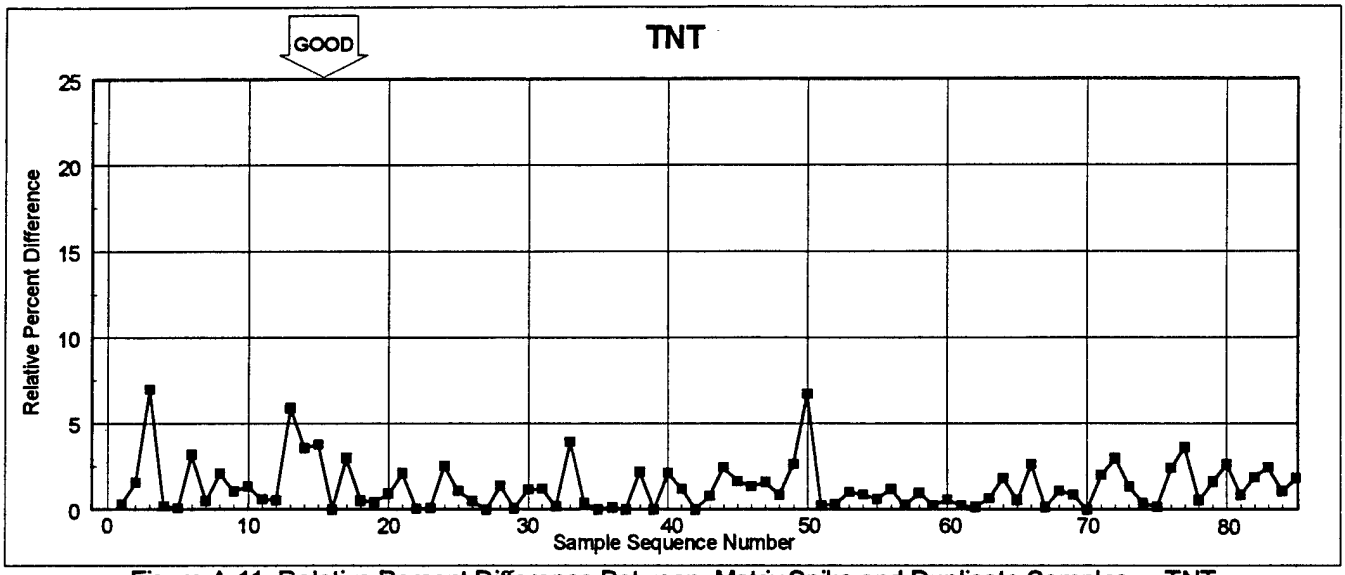

Figure A-11 Relative Percent Difference Between Matrix Spike and Duplicate Samples - TNT

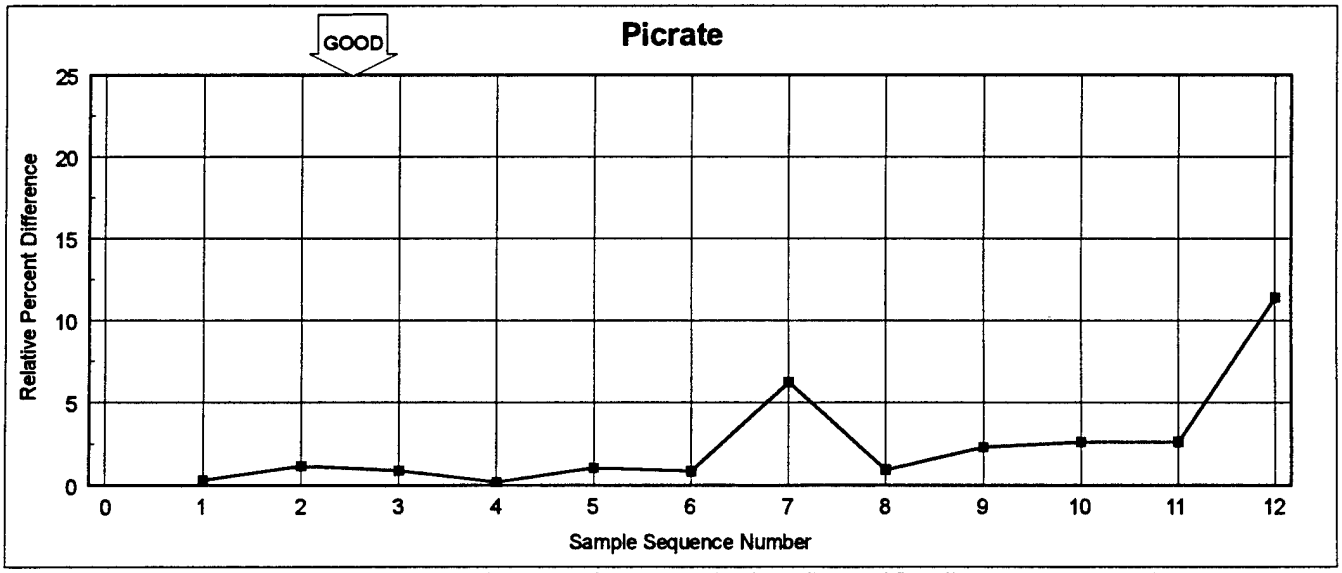

Figure A-12 Relative Percent Difference Between Matrix Spike and Duplicate Samples - Picrate

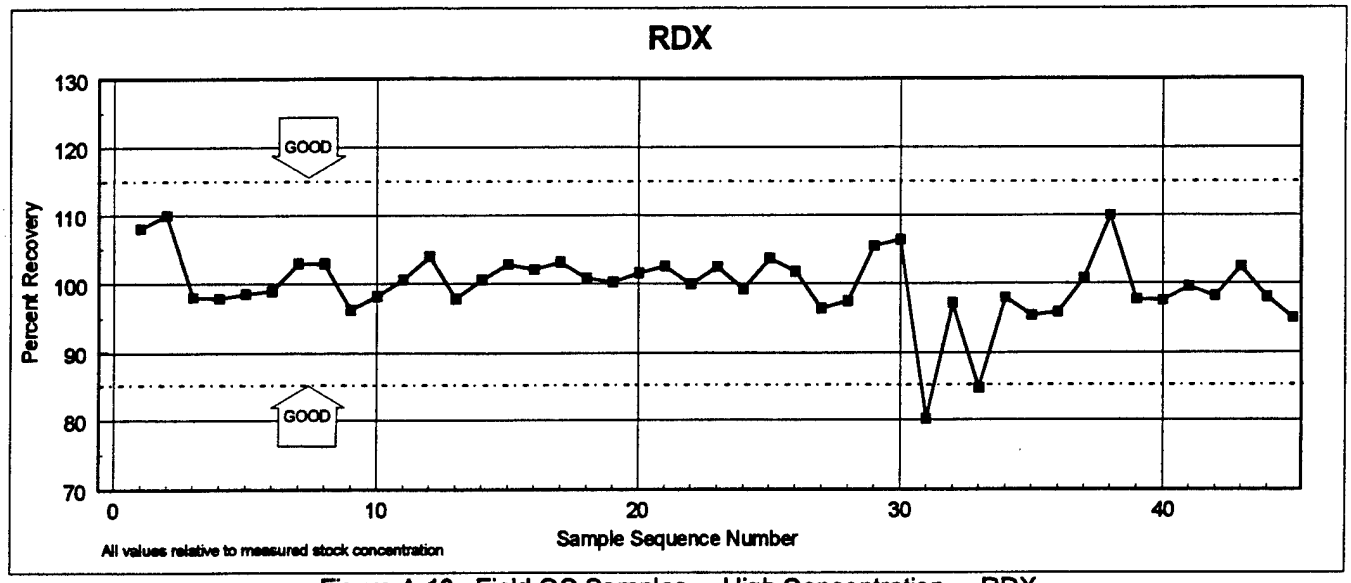

Figure A-13 Field QC Samples - High Concentration - RDX

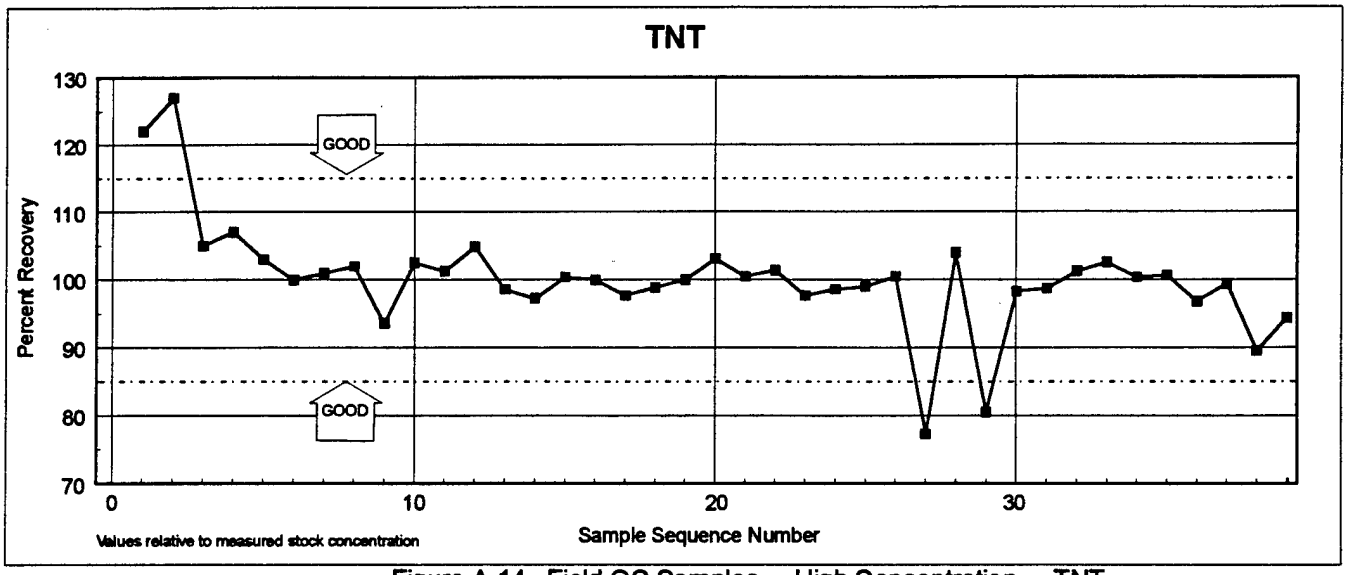

Figure A-14 Field QC Samples - High Concentration - TNT

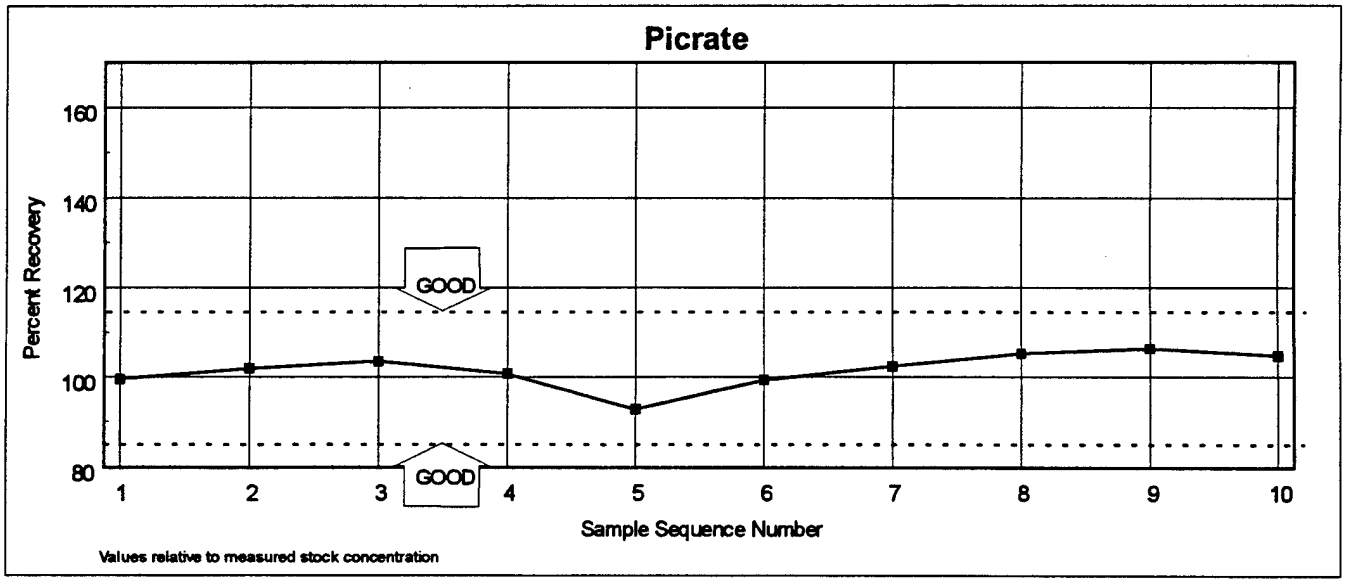

Figure A-15 Field QC Samples - High Concentration - Picrate

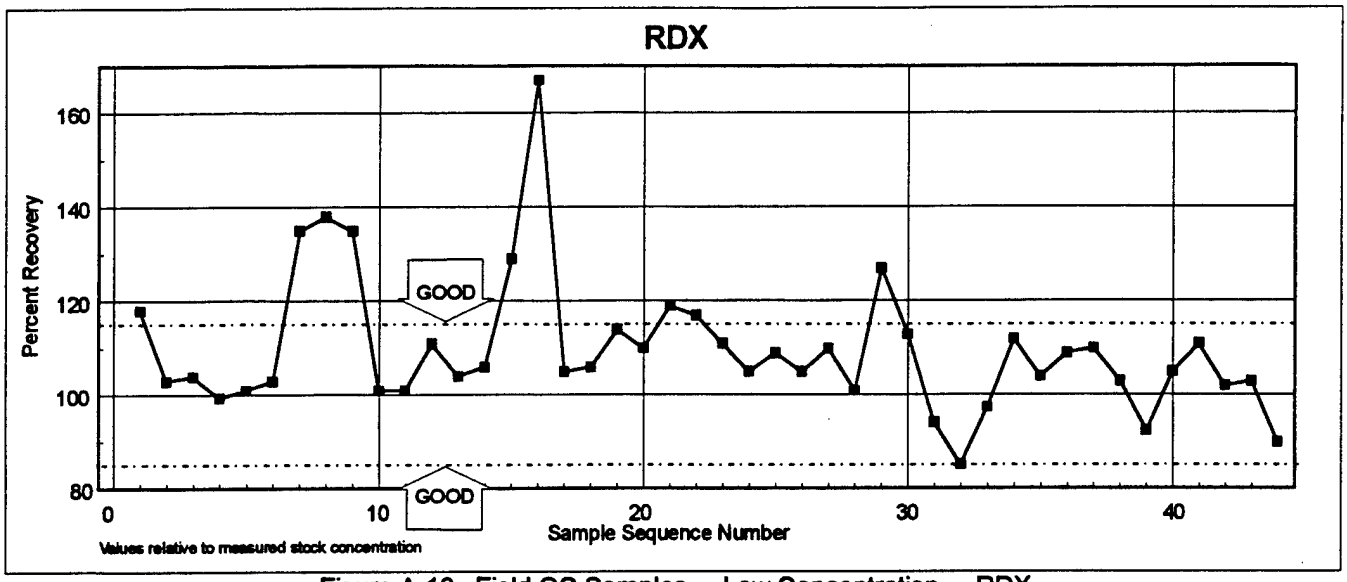

Figure A-16 Field QC Samples - Low Concentration - RDX

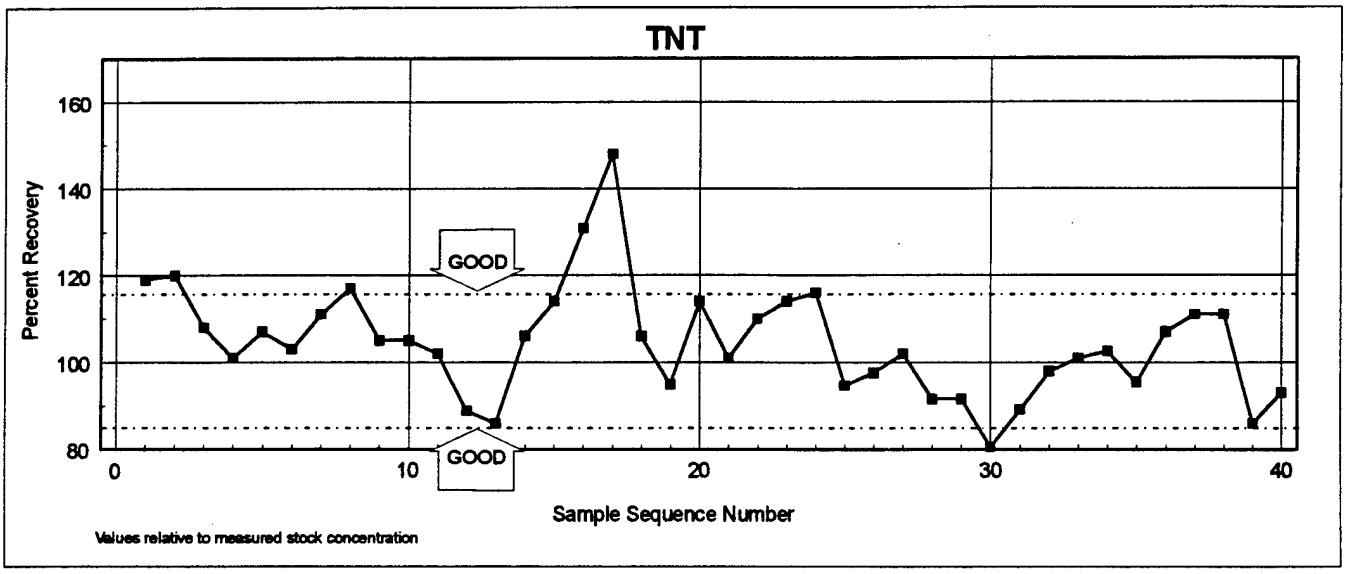

Figure A-17 Field QC Samples - Low Concentration - TNT

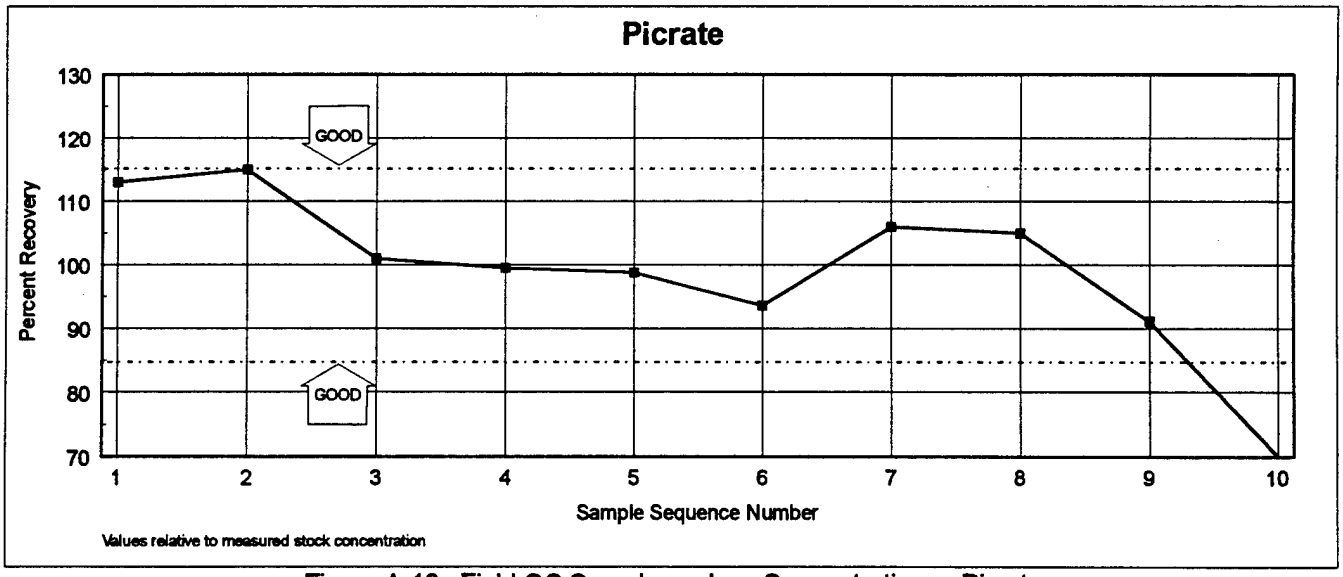

Figure A-18 Field QC Samples - Low Concentration - Picrate

APPENDIX B

METHODS AND PROCEDURES

METHODS AND PROCEDURES

APPENDIX B1

QUALITY ASSURANCE

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CHAPTER ONE
QUALITY CONTROL

1.0 INTRODUCTION

It is the goal of the U.S. Environmental Protection Agency's (EPA's) quality assurance (QA) program to ensure that all data be scientifically valid, defensible, and of known precision and accuracy. The data should be of sufficient known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. The QA program is management's tool for achieving this goal.

For RCRA analyses, the recommended minimum requirements for a QA program and the associated quality control (QC) procedures are provided in this chapter.

The data acquired from QC procedures are used to estimate the quality of analytical data, to determine the need for corrective action in response to identified deficiencies, and to interpret results after corrective action procedures are implemented. Method-specific QC procedures are incorporated in the individual methods since they are not applied universally.

A total program to generate data of acceptable quality should include both a QA component, which encompasses the management procedures and controls, as well as an operational day-to-day QC component. This chapter defines fundamental elements of such a data collection program. Data collection efforts involve:

1. design of a project plan to achieve the data quality objectives (DQOs);

2. implementation of the project plan; and

3. assessment of the data to determine if the DQOs are met.

The project plan may be a sampling and analysis plan or a waste analysis plan if it covers the QA/QC goals of the Chapter, or it may be a Quality Assurance Project Plan as described later in this chapter.

This chapter identifies the minimal QC components that should be used in the performance of sampling and analyses, including the QC information which should be documented. Guidance is provided to construct QA programs for field and laboratory work conducted in support of the RCRA program.

2.0 QA PROJECT PLAN

It is recommended that all projects which generate environment-related data in support of RCRA have a QA Project Plan (QAPjP) or equivalent. In some instances, a sampling and analysis plan or a waste analysis plan may be equivalent if it covers all of the QA/QC goals outlined in this chapter. In addition, a separate QAPjP need not be prepared for routine analyses or activities where the procedures to be followed are described in a Standard

Operating Procedures manual or similar document and include the elements of a QAPjP. These documents should be available and referenced in the documentation and/or records for the analysis activities. The term "QAPjP" in this chapter refers to any of these QA/QC documents.

The QAPjP should detail the QA/QC goals and protocols for a specific data collection activity. The QAPjP sets forth a plan for sampling and analysis activities that will generate data of a quality commensurate with their intended use. QAPjP elements should include a description of the project and its objectives; a statement of the DQOs of the project; identification of those involved in the data collection and their responsibilities and authorities; reference to (or inclusion of) the specific sample collection and analysis procedures that will be followed for all aspects of the project; enumeration of QC procedures to be followed; and descriptions of all project documentation. Additional elements should be included in the QAPjP if needed to address all quality related aspects of the data collection project. Elements should be omitted only when they are inappropriate for the project or when absence of those elements will not affect the quality of data obtained for the project (see reference 1).

The role and importance of DQOs and project documentation are discussed below in Sections 2.1 through 2.6. Management and organization play a critical role in determining the effectiveness of a QA/QC program and ensuring that all required procedures are followed. Section 2.7 discusses the elements of an organization's QA program that have been found to ensure an effective program. Field operations and laboratory operations (along with applicable QC procedures) are discussed in Sections 3 and 4, respectively.

2.1 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) for the data collection activity describe the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data. This uncertainty is used to specify the quality of the measurement data required, usually in terms of objectives for precision, bias, representativeness, comparability and completeness. The DQOs should be defined prior to the initiation of the field and laboratory work. The field and laboratory organizations performing the work should be aware of the DQOs so that their personnel may make informed decisions during the course of the project to attain those DQOs. More detailed information on DQOs is available from the U.S. EPA Quality Assurance Management Staff (QAMS) (see references 2 and 4).

2.2 PROJECT OBJECTIVES

A statement of the project objectives and how the objectives are to be attained should be concisely stated and sufficiently detailed to permit clear understanding by all parties involved in the data collection effort. This includes a statement of what problem is to be solved and the information required

in the process. It also includes appropriate statements of the DQOs (i.e., the acceptable level of uncertainty in the information).

2.3 SAMPLE COLLECTION

Sampling procedures, locations, equipment, and sample preservation and handling requirements should be specified in the QAPjP. Further details on quality assurance procedures for field operations are described in Section 3 of this chapter. The OSW is developing policies and procedures for sampling in a planned revision of Chapter Nine of this manual. Specific procedures for groundwater sampling are provided in Chapter Eleven of this manual.

2.4 ANALYSIS AND TESTING

Analytes and properties of concern, analytical and testing procedures to be employed, required detection limits, and requirements for precision and bias should be specified. All applicable regulatory requirements and the project DQOs should be considered when developing the specifications. Further details on the procedures for analytical operations are described in Section 4 of this chapter.

2.5 QUALITY CONTROL

The quality assurance program should address both field and laboratory activities. Quality control procedures should be specified for estimating the precision and bias of the data. Recommended minimum requirements for QC samples have been established by EPA and should be met in order to satisfy recommended minimum criteria for acceptable data quality. Further details on procedures for field and laboratory operations are described in Sections 3 and 4, respectively, of this chapter.

2.6 PROJECT DOCUMENTATION

Documents should be prepared and maintained in conjunction with the data collection effort. Project documentation should be sufficient to allow review of all aspects of the work being performed. The QAPjP discussed in Sections 3 and 4 is one important document that should be maintained.

The length of storage time for project records should comply with regulatory requirements, organizational policy, or project requirements, whichever is more stringent. It is recommended that documentation be stored for three years from submission of the project final report.

Documentation should be secured in a facility that adequately addresses/minimizes its deterioration for the length of time that it is to be retained. A system allowing for the expedient retrieval of information should exist.

Access to archived information should be controlled to maintain the integrity of the data. Procedures should be developed to identify those individuals with access to the data.

2.7 ORGANIZATION PERFORMING FIELD OR LABORATORY OPERATIONS

Proper design and structure of the organization facilitates effective and efficient transfer of information and helps to prevent important procedures from being overlooked.

The organizational structure, functional responsibilities, levels of authority, job descriptions, and lines of communication for all project activities should be established and documented. One person may cover more than one organizational function. Each project participant should have a clear understanding of his or her duties and responsibilities and the relationship of those responsibilities to the overall data collection effort.

The management of each organization participating in a project involving data collection activities should establish that organization's operational and QA policies. This information should be documented in the QAPjP. The management should ensure that (1) the appropriate methodologies are followed as documented in the QAPjPs; (2) personnel clearly understand their duties and responsibilities; (3) each staff member has access to appropriate project documents; (4) any deviations from the QAPjP are communicated to the project management and documented; and (5) communication occurs between the field, laboratory, and project management, as specified in the QAPjP. In addition, each organization should ensure that their activities do not increase the risk to humans or the environment at or about the project location. Certain projects may require specific policies or a Health and Safety Plan to provide this assurance.

The management of the participating field or laboratory organization should establish personnel qualifications and training requirements for the project. Each person participating in the project should have the education, training, technical knowledge, and experience, or a combination thereof, to enable that individual to perform assigned functions. Training should be provided for each staff member as necessary to perform their functions properly. Personnel qualifications should be documented in terms of education, experience, and training, and periodically reviewed to ensure adequacy to current responsibilities.

Each participating field organization or laboratory organization should have a designated QA function (i.e., a team or individual trained in QA) to monitor operations to ensure that the equipment, personnel, activities, procedures, and documentation conform with the QAPjP. To the extent possible, the QA monitoring function should be entirely separate from, and independent of, personnel engaged in the work being monitored. The QA function should be responsible for the QA review.

2.7.1 Performance Evaluation

Performance evaluation studies are used to measure the performance of the laboratory on unknown samples. Performance evaluation samples are typically submitted to the laboratory as blind samples by an independent outside source. The results are compared to predetermined acceptance limits. Performance evaluation samples can also be submitted to the laboratory as part of the QA function during internal assessment of laboratory performance. Records of all performance evaluation studies should be maintained by the laboratory. Problems identified through participation in performance evaluation studies should be immediately investigated and corrected.

2.7.2 Internal Assessment by QA Function

Personnel performing field and laboratory activities are responsible for continually monitoring individual compliance with the QAPjP. The QA function should review procedures, results and calculations to determine compliance with the QAPjP. The results of this internal assessment should be reported to management with requirements for a plan to correct observed deficiencies.

2.7.3 External Assessment

The field and laboratory activities may be reviewed by personnel external to the organization. Such an assessment is an extremely valuable method for identifying overlooked problems. The results of the external assessment should be submitted to management with requirements for a plan to correct observed deficiencies.

2.7.4 On-Site Evaluation

On-site evaluations may be conducted as part of both internal and external assessments. The focus of an on-site evaluation is to evaluate the degree of conformance of project activities with the applicable QAPjP. On-site evaluations may include, but are not limited to, a complete review of facilities, staff, training, instrumentation, procedures, methods, sample collection, analyses, QA policies and procedures related to the generation of environmental data. Records of each evaluation should include the date of the evaluation, location, the areas reviewed, the person performing the evaluation, findings and problems, and actions recommended and taken to resolve problems. Any problems identified that are likely to affect data integrity should be brought immediately to the attention of management.

2.7.4.1 Field Activities

The review of field activities should be conducted by one or more persons knowledgeable in the activities being reviewed and include evaluating, at a minimum, the following subjects:

Completeness of Field Reports -- This review determines whether all requirements for field activities in the QAPjP have been fulfilled, that complete records exist for each field activity, and that the procedures

specified in the QAPjP have been implemented. Emphasis on field documentation will help assure sample integrity and sufficient technical information to recreate each field event. The results of this completeness check should be documented, and environmental data affected by incomplete records should be identified.

Identification of Valid Samples -- This review involves interpretation and evaluation of the field records to detect problems affecting the representativeness of environmental samples. Examples of items that might indicate potentially invalid samples include improper well development, improperly screened wells, instability of pH or conductivity, and collection of volatiles near internal combustion engines. The field records should be evaluated against the QAPjP and SOPs. The reviewer should document the sample validity and identify the environmental data associated with any poor or incorrect field work.

Correlation of Field Test Data -- This review involves comparing any available results of field measurements obtained by more than one method. For example, surface geophysical methods should correlate with direct methods of site geologic characterization such as lithologic logs constructed during drilling operations.

Identification of Anomalous Field Test Data -- This review identifies any anomalous field test data. For example, a water temperature for one well that is 5 degrees higher than any other well temperature in the same aquifer should be noted. The reviewer should evaluate the impact of anomalous field measurement results on the associated environmental data.

Validation of Field Analyses -- This review validates and documents all data from field analysis that are generated *in situ* or from a mobile laboratory as specified in Section 2.7.4.2. The reviewer should document whether the QC checks meet the acceptance criteria, and whether corrective actions were taken for any analysis performed when acceptance criteria were exceeded.

2.7.4.2 Laboratory Activities

The review of laboratory data should be conducted by one or more persons knowledgeable in laboratory activities and include evaluating, at a minimum, the following subjects:

Completeness of Laboratory Records -- This review determines whether: (1) all samples and analyses required by the QAPjP have been processed, (2) complete records exist for each analysis and the associated QC samples, and that (3) the procedures specified in the QAPjP have been implemented. The results of the completeness check should be documented, and environmental data affected by incomplete records should be identified.

Evaluation of Data with Respect to Detection and Quantitation Limits -- This review compares analytical results to required quantitation limits. Reviewers should document instances where detection or quantitation limits

exceed regulatory limits, action levels, or target concentrations specified in the QAPjP.

Evaluation of Data with Respect to Control Limits -- This review compares the results of QC and calibration check samples to control criteria. Corrective action should be implemented for data not within control limits. The reviewer should check that corrective action reports, and the results of reanalysis, are available. The review should determine whether samples associated with out-of-control QC data are identified in a written record of the data review, and whether an assessment of the utility of such analytical results is recorded.

Review of Holding Time Data -- This review compares sample holding times to those required by the QAPjP, and notes all deviations.

Review of Performance Evaluation (PE) Results -- PE study results can be helpful in evaluating the impact of out-of-control conditions. This review documents any recurring trends or problems evident in PE studies and evaluates their effect on environmental data.

Correlation of Laboratory Data -- This review determines whether the results of data obtained from related laboratory tests, e.g., Purgeable Organic Halides (POX) and Volatile Organics, are documented, and whether the significance of any differences is discussed in the reports.

2.7.5 QA Reports

There should be periodic reporting of pertinent QA/QC information to the project management to allow assessment of the overall effectiveness of the QA program. There are three major types of QA reports to project management:

Periodic Report on Key QA Activities -- Provides summary of key QA activities during the period, stressing measures that are being taken to improve data quality; describes significant quality problems observed and corrective actions taken; reports information regarding any changes in certification/accreditation status; describes involvement in resolution of quality issues with clients or agencies; reports any QA organizational changes; and provides notice of the distribution of revised documents controlled by the QA organization (i.e., procedures).

Report on Measurement Quality Indicators -- Includes the assessment of QC data gathered over the period, the frequency of analyses repeated due to unacceptable QC performance, and, if possible, the reason for the unacceptable performance and corrective action taken.

Reports on QA Assessments -- Includes the results of the assessments and the plan for correcting identified deficiencies; submitted immediately following any internal or external on-site evaluation or upon receipt of the results of any performance evaluation studies.

3.0 FIELD OPERATIONS

The field operations should be conducted in such a way as to provide reliable information that meets the DQOs. To achieve this, certain minimal policies and procedures should be implemented. The OSW is considering revisions of Chapter Nine and Eleven of this manual. Supplemental information and guidance is available in the RCRA Ground-Water Monitoring Technical Enforcement Guidance Document (TEGD) (Reference 3). The project documentation should contain the information specified below.

3.1 FIELD LOGISTICS

The QAPjP should describe the type(s) of field operations to be performed and the appropriate area(s) in which to perform the work. The QAPjP should address ventilation, protection from extreme weather and temperatures, access to stable power, and provision for water and gases of required purity.

Whenever practical, the sampling site facilities should be examined prior to the start of work to ensure that all required items are available. The actual area of sampling should be examined to ensure that trucks, drilling equipment, and personnel have adequate access to the site.

The determination as to whether sample shipping is necessary should be made during planning for the project. This need is established by evaluating the analyses to be performed, sample holding times, and location of the site and the laboratory. Shipping or transporting of samples to a laboratory should be done within a timeframe such that recommended holding times are met.

Samples should be packaged, labelled, preserved (e.g., preservative added, iced, etc.), and documented in an area which is free of contamination and provides for secure storage. The level of custody and whether sample storage is needed should be addressed in the QAPjP.

Storage areas for solvents, reagents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability prior to use.

Decontamination of sampling equipment may be performed at the location where sampling occurs, prior to going to the sampling site, or in designated areas near the sampling site. Project documentation should specify where and how this work is accomplished. If decontamination is to be done at the site, water and solvents of appropriate purity should be available. The method of accomplishing decontamination, including the required materials, solvents, and water purity should be specified.

During the sampling process and during on-site or <u>in situ</u> analyses, waste materials are sometimes generated. The method for storage and disposal of these waste materials that complies with applicable local, state and Federal regulations should be specified. Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so

as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage for field records, and the measures to ensure the integrity of the data should be specified.

3.2 EQUIPMENT/INSTRUMENTATION

The equipment, instrumentation, and supplies at the sampling site should be specified and should be appropriate to accomplish the activities planned. The equipment and instrumentation should meet the requirements of specifications, methods, and procedures as specified in the QAPjP.

3.3 OPERATING PROCEDURES

The QAPjP should describe or make reference to all field activities that may affect data quality. For routinely performed activities, standard operating procedures (SOPs) are often prepared to ensure consistency and to save time and effort in preparing QAPjPs. Any deviation from an established procedure during a data collection activity should be documented. The procedures should be available for the indicated activities, and should include, at a minimum, the information described below.

3.3.1 Sample Management

The numbering and labeling system, chain-of-custody procedures, and how the samples are to be tracked from collection to shipment or receipt by the laboratory should be specified. Sample management procedures should also specify the holding times, volumes of sample required by the laboratory, required preservatives, and shipping requirements.

3.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and record keeping for stocks and dilutions should be included.

3.3.3 Decontamination

The procedures describing decontamination of field equipment before and during the sample collection process should be specified. These procedures should include cleaning materials used, the order of washing and rinsing with the cleaning materials, requirements for protecting or covering cleaned equipment, and procedures for disposing of cleaning materials.

3.3.4 Sample Collection

The procedures describing how the sampling operations are actually performed in the field should be specified. A simple reference to standard methods is not sufficient, unless a procedure is performed exactly as described in the published method. Methods from source documents published by the EPA, American Society for Testing and Materials, U.S. Department of the Interior, National Water Well Association, American Petroleum Institute, or other recognized organizations with appropriate expertise should be used, if possible. The procedures for sample collection should include at least the following:

- Applicability of the procedure,
- Equipment required,
- Detailed description of procedures to be followed in collecting the samples,
- Common problems encountered and corrective actions to be followed, and
- Precautions to be taken.

3.3.5 Field Measurements

The procedures describing all methods used in the field to determine a chemical or physical parameter should be described in detail. The procedures should address criteria from Section 4, as appropriate.

3.3.6 Equipment Calibration And Maintenance

The procedures describing how to ensure that field equipment and instrumentation are in working order should be specified. These describe calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, and service arrangements for equipment. Calibration and maintenance of field equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

3.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the sample collection process should be specified. These should include specific steps to take in correcting deficiencies such as performing additional decontamination of equipment, resampling, or additional training of field personnel. The procedures should specify that each corrective action should be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

3.3.8 Data Reduction and Validation

The procedures describing how to compute results from field measurements and to review and validate these data should be specified. They should include all formulas used to calculate results and procedures used to independently verify that field measurement results are correct.

3.3.9 Reporting

The procedures describing the process for reporting the results of field activities should be specified.

3.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving project-specific records and field operations records should be specified. These procedures should detail record generation and control and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records relate to field work performed for a project. These records may include correspondence, chain-of-custody records, field notes, all reports issued as a result of the work, and procedures used.

Field operations records document overall field operations and may include equipment performance and maintenance logs, personnel files, general field procedures, and corrective action reports.

3.3.11 Waste Disposal

The procedures describing the methods for disposal of waste materials resulting from field operations should be specified.

3.4 FIELD QA AND QC REQUIREMENTS

The QAPjP should describe how the following elements of the field QC program will be implemented.

3.4.1 Control Samples

Control samples are QC samples that are introduced into a process to monitor the performance of the system. Control samples, which may include blanks (e.g., trip, equipment, and laboratory), duplicates, spikes, analytical standards, and reference materials, can be used in different phases of the data collection process beginning with sampling and continuing through transportation, storage, and analysis.

Each day of sampling, at least one field duplicate and one equipment rinsate should be collected for each matrix sampled. If this frequency is not appropriate for the sampling equipment and method, then the appropriate changes

should be clearly identified in the QAPjP. When samples are collected for volatile organic analysis, a trip blank is also recommended for each day that samples are collected. In addition, for each sampling batch (20 samples of one matrix type), enough volume should be collected for at least one sample so as to allow the laboratory to prepare one matrix spike and either one matrix duplicate or one matrix spike duplicate for each analytical method employed. This means that the following control samples are recommended:

- Field duplicate (one per day per matrix type)
- Equipment rinsate (one per day per matrix type)
- Trip blank (one per day, volatile organics only)
- Matrix spike (one per batch [20 samples of each matrix type])
- Matrix duplicate or matrix spike duplicate (one per batch)

Additional control samples may be necessary in order to assure data quality to meet the project-specific DQOs.

3.4.2 Acceptance Criteria

Procedures should be in place for establishing acceptance criteria for field activities described in the QAPjP. Acceptance criteria may be qualitative or quantitative. Field events or data that fall outside of established acceptance criteria may indicate a problem with the sampling process that should be investigated.

3.4.3 Deviations

All deviations from plan should be documented as to the extent of, and reason for, the deviation. Any activity not performed in accordance with procedures or QAPjPs is considered a deviation from plan. Deviations from plan may or may not affect data quality.

3.4.4 Corrective Action

Errors, deficiencies, deviations, certain field events, or data that fall outside established acceptance criteria should be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the system. The investigation of the problem and any subsequent corrective action taken should be documented.

3.4.5 Data Handling

All field measurement data should be reduced according to protocols described or referenced in the QAPjP. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations should be recorded to enable reconstruction of the final result at a later date.

Data should be reported in accordance with the requirements of the end-user as described in the QAPjP.

3.5 QUALITY ASSURANCE REVIEW

The QA Review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that field staff conform to these procedures. QA review should be conducted as deemed appropriate and necessary.

3.6 FIELD RECORDS

Records provide the direct evidence and support for the necessary technical interpretations, judgments, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support current or ongoing technical studies and activities and should provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable and protected against damage, deterioration, or loss. The discussion in this section (3.6) outlines recommended procedures for record keeping. Organizations which conduct field sampling should develop appropriate record keeping procedures which satisfy relevant technical and legal requirements.

Field records generally consist of bound field notebooks with prenumbered pages, sample collection forms, personnel qualification and training forms, sample location maps, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and field change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising field records should be clearly defined, with the lines of authority included. It is recommended that all documentation errors should be corrected by drawing a single line through the error so it remains legible and should be initialed by the responsible individual, along with the date of change. The correction should be written adjacent to the error.

Records should include (but are not limited to) the following:

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include provisions for documentation of frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy of all working standards against primary grade standards should be routinely followed.

Sample Collection -- To ensure maximum utility of the sampling effort and resulting data, documentation of the sampling protocol, as performed in the field, is essential. It is recommended that sample collection records contain, at a minimum, the names of persons conducting the activity, sample number, sample location, equipment used, climatic conditions, documentation of adherence to protocol, and unusual observations. The

actual sample collection record is usually one of the following: a bound field notebook with prenumbered pages, a pre-printed form, or digitized information on a computer tape or disc.

Chain-of-Custody Records -- The chain-of-custody involving the possession of samples from the time they are obtained until they are disposed or shipped off-site should be documented as specified in the QAPjP and should include the following information: (1) the project name; (2) signatures of samplers; (3) the sample number, date and time of collection, and grab or composite sample designation; (4) signatures of individuals involved in sample transfer; and (5) if applicable, the air bill or other shipping number.

Maps and Drawings -- Project planning documents and reports often contain maps. The maps are used to document the location of sample collection points and monitoring wells and as a means of presenting environmental data. Information used to prepare maps and drawings is normally obtained through field surveys, property surveys, surveys of monitoring wells, aerial photography or photogrammetric mapping. The final, approved maps and/or drawings should have a revision number and date and should be subject to the same controls as other project records.

QC Samples -- Documentation for generation of QC samples, such as trip and equipment rinsate blanks, duplicate samples, and any field spikes should be maintained.

Deviations -- All deviations from procedural documents and the QAPjP should be recorded in the site logbook.

Reports -- A copy of any report issued and any supporting documentation should be retained.

4.0 LABORATORY OPERATIONS

The laboratory should conduct its operations in such a way as to provide reliable information. To achieve this, certain minimal policies and procedures should be implemented.

4.1 FACILITIES

The QAPjP should address all facility-related issues that may impact project data quality. Each laboratory should be of suitable size and construction to facilitate the proper conduct of the analyses. Adequate bench space or working area per analyst should be provided. The space requirement per analyst depends on the equipment or apparatus that is being utilized, the number of samples that the analyst is expected to handle at any one time, and the number of operations that are to be performed concurrently by a single analyst. Other issues to be considered include, but are not limited to, ventilation, lighting,

control of dust and drafts, protection from extreme temperatures, and access to a source of stable power.

Laboratories should be designed so that there is adequate separation of functions to ensure that no laboratory activity has an adverse effect on the analyses. The laboratory may require specialized facilities such as a perchloric acid hood or glovebox.

Separate space for laboratory operations and appropriate ancillary support should be provided, as needed, for the performance of routine and specialized procedures.

As necessary to ensure secure storage and prevent contamination or misidentification, there should be adequate facilities for receipt and storage of samples. The level of custody required and any special requirements for storage such as refrigeration should be described in planning documents.

Storage areas for reagents, solvents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability.

Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage of laboratory records and the measures to ensure the integrity of the data should be specified.

4.2 EQUIPMENT/INSTRUMENTATION

Equipment and instrumentation should meet the requirements and specifications of the specific test methods and other procedures as specified in the QAPjP. The laboratory should maintain an equipment/instrument description list that includes the manufacturer, model number, year of purchase, accessories, and any modifications, updates, or upgrades that have been made.

4.3 OPERATING PROCEDURES

The QAPjP should describe or make reference to all laboratory activities that may affect data quality. For routinely performed activities, SOPs are often prepared to ensure consistency and to save time and effort in preparing QAPjPs. Any deviation from an established procedure during a data collection activity should be documented. It is recommended that procedures be available for the indicated activities, and include, at a minimum, the information described below.

4.3.1 Sample Management

The procedures describing the receipt, handling, scheduling, and storage of samples should be specified.

Sample Receipt and Handling -- These procedures describe the precautions to be used in opening sample shipment containers and how to verify that chain-of-custody has been maintained, examine samples for damage, check for proper preservatives and temperature, and log samples into the laboratory sample streams.

Sample Scheduling -- These procedures describe the sample scheduling in the laboratory and includes procedures used to ensure that holding time requirements are met.

Sample Storage -- These procedures describe the storage conditions for all samples, verification and documentation of daily storage temperature, and how to ensure that custody of the samples is maintained while in the laboratory.

4.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and recordkeeping for stocks and dilutions should be included.

4.3.3 General Laboratory Techniques

The procedures describing all essentials of laboratory operations that are not addressed elsewhere should be specified. These techniques should include, but are not limited to, glassware cleaning procedures, operation of analytical balances, pipetting techniques, and use of volumetric glassware.

4.3.4 Test Methods

Procedures for test methods describing how the analyses are actually performed in the laboratory should be specified. A simple reference to standard methods is not sufficient, unless the analysis is performed exactly as described in the published method. Whenever methods from SW-846 are not appropriate, recognized methods from source documents published by the EPA, American Public Health Association (APHA), American Society for Testing and Materials (ASTM), the National Institute for Occupational Safety and Health (NIOSH), or other recognized organizations with appropriate expertise should be used, if possible. The documentation of the actual laboratory procedures for analytical methods should include the following:

Sample Preparation and Analysis Procedures -- These include applicable holding time, extraction, digestion, or preparation steps as appropriate to the method; procedures for determining the appropriate dilution to

analyze; and any other information required to perform the analysis accurately and consistently.

Instrument Standardization -- This includes concentration(s) and frequency of analysis of calibration standards, linear range of the method, and calibration acceptance criteria.

Sample Data -- This includes recording requirements and documentation including sample identification number, analyst, data verification, date of analysis and verification, and computational method(s).

Precision and Bias -- This includes all analytes for which the method is applicable and the conditions for use of this information.

Detection and Reporting Limits -- This includes all analytes in the method.

Test-Specific QC -- This describes QC activities applicable to the specific test and references any applicable QC procedures.

4.3.5 Equipment Calibration and Maintenance

The procedures describing how to ensure that laboratory equipment and instrumentation are in working order should be specified. These procedures include calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, service arrangements for all equipment, and spare parts available in-house. Calibration and maintenance of laboratory equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

4.3.6 QC

The type, purpose, and frequency of QC samples to be analyzed in the laboratory and the acceptance criteria should be specified. Information should include the applicability of the QC sample to the analytical process, the statistical treatment of the data, and the responsibility of laboratory staff and management in generating and using the data. Further details on development of project-specific QC protocols are described in Section 4.4.

4.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the analytical process should be specified. These should include specific steps to take in correcting the deficiencies such as preparation of new standards and reagents, recalibration and restandardization of equipment, reanalysis of samples, or additional training of laboratory personnel in methods and procedures. The procedures should specify that each corrective action should be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

4.3.8 Data Reduction and Validation

The procedures describing how to review and validate the data should be specified. They should include procedures for computing and interpreting the results from QC samples, and independent procedures to verify that the analytical results are reported correctly. In addition, routine procedures used to monitor precision and bias, including evaluations of reagent, equipment rinsate, and trip blanks, calibration standards, control samples, duplicate and matrix spike samples, and surrogate recovery, should be detailed in the procedures. More detailed validation procedures should be performed when required in the contract or QAPjP.

4.3.9 Reporting

The procedures describing the process for reporting the analytical results should be specified.

4.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving laboratory records should be specified. The procedures should detail record generation and control, and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records may include correspondence, chain-of-custody records, request for analysis, calibration data records, raw and finished analytical and QC data, data reports, and procedures used.

Laboratory operations records may include laboratory notebooks, instrument performance logs and maintenance logs in bound notebooks with prenumbered pages; laboratory benchsheets; software documentation; control charts; reference material certification; personnel files; laboratory procedures; and corrective action reports.

4.3.11 Waste Disposal

The procedures describing the methods for disposal of chemicals including standard and reagent solutions, process waste, and samples should be specified.

4.4 LABORATORY QA AND QC PROCEDURES

The QAPjP should describe how the following required elements of the laboratory QC program are to be implemented.

4.4.1 Method Proficiency

Procedures should be in place for demonstrating proficiency with each analytical method routinely used in the laboratory. These should include procedures for demonstrating the precision and bias of the method as performed by the laboratory and procedures for determining the method detection limit

(MDL). All terminology, procedures and frequency of determinations associated with the laboratory's establishment of the MDL and the reporting limit should be well-defined and well-documented. Documented precision, bias, and MDL information should be maintained for all methods performed in the laboratory.

4.4.2 Control Limits

Procedures should be in place for establishing and updating control limits for analysis. Control limits should be established to evaluate laboratory precision and bias based on the analysis of control samples. Typically, control limits for bias are based on the historical mean recovery plus or minus three standard deviation units, and control limits for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units. Procedures should be in place for monitoring historical performance and should include graphical (control charts) and/or tabular presentations of the data.

4.4.3 Laboratory Control Procedures

Procedures should be in place for demonstrating that the laboratory is in control during each data collection activity. Analytical data generated with laboratory control samples that fall within prescribed limits are judged to be generated while the laboratory was in control. Data generated with laboratory control samples that fall outside the established control limits are judged to be generated during an "out-of-control" situation. These data are considered suspect and should be repeated or reported with qualifiers.

Laboratory Control Samples -- Laboratory control samples should be analyzed for each analytical method when appropriate for the method. A laboratory control sample consists of either a control matrix spiked with analytes representative of the target analytes or a certified reference material.

Laboratory control sample(s) should be analyzed with each batch of samples processed to verify that the precision and bias of the analytical process are within control limits. The results of the laboratory control sample(s) are compared to control limits established for both precision and bias to determine usability of the data.

Method Blank -- When appropriate for the method, a method blank should be analyzed with each batch of samples processed to assess contamination levels in the laboratory. Guidelines should be in place for accepting or rejecting data based on the level of contamination in the blank.

Procedures should be in place for documenting the effect of the matrix on method performance. When appropriate for the method, there should be at least one matrix spike and either one matrix duplicate or one matrix spike duplicate per analytical batch. Additional control samples may be necessary to assure data quality to meet the project-specific DQOs.

Matrix-Specific Bias -- Procedures should be in place for determining the bias of the method due to the matrix. These procedures should include preparation and analysis of matrix spikes, selection and use of surrogates for organic methods, and the method of standard additions for metal and inorganic methods. When the concentration of the analyte in the sample is greater than 0.1%, no spike is necessary.

Matrix-Specific Precision -- Procedures should be in place for determining the precision of the method for a specific matrix. These procedures should include analysis of matrix duplicates and/or matrix spike duplicates. The frequency of use of these techniques should be based on the DQO for the data collection activity.

Matrix-Specific Detection Limit -- Procedures should be in place for determining the MDL for a specific matrix type (e.g., wastewater treatment sludge, contaminated soil, etc).

4.4.4 Deviations

Any activity not performed in accordance with laboratory procedures or QAPjPs is considered a deviation from plan. All deviations from plan should be documented as to the extent of, and reason for, the deviation.

4.4.5 Corrective Action

Errors, deficiencies, deviations, or laboratory events or data that fall outside of established acceptance criteria should be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the analytical system. The investigation of the problem and any subsequent corrective action taken should be documented.

4.4.6 Data Handling

Data resulting from the analyses of samples should be reduced according to protocols described in the laboratory procedures. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, and blank- or background-correction protocols) should be recorded in order to enable reconstruction of the final result at a later date. Information on the preparation of the sample (e.g., weight or volume of sample used, percent dry weight for solids, extract volume, dilution factor used) should also be maintained in order to enable reconstruction of the final result at a later date.

All data should be reviewed by a second analyst or supervisor according to laboratory procedures to ensure that calculations are correct and to detect transcription errors. Spot checks should be performed on computer calculations to verify program validity. Errors detected in the review process should be referred to the analyst(s) for corrective action. Data should be reported in accordance with the requirements of the end-user. It is recommended that the supporting documentation include at a minimum:

- Laboratory name and address.
- Sample information (including unique sample identification, sample collection date and time, date of sample receipt, and date(s) of sample preparation and analysis).
- Analytical results reported with an appropriate number of significant figures.
- Detection limits that reflect dilutions, interferences, or correction for equivalent dry weight.
- Method reference.
- Appropriate QC results (correlation with sample batch should be traceable and documented).
- Data qualifiers with appropriate references and narrative on the quality of the results.

4.5 QUALITY ASSURANCE REVIEW

The QA review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that laboratory staff conform to these procedures. QA review should be conducted as deemed appropriate and necessary.

4.6 LABORATORY RECORDS

Records provide the direct evidence and support for the necessary technical interpretations, judgements, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support technical studies and activities, and provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable, and protected against damage, deterioration, or loss. The discussion in this section (4.6) outlines recommended procedures for record keeping. Organizations which conduct field sampling should develop appropriate record keeping procedures which satisfy relevant technical and legal requirements.

Laboratory records generally consist of bound notebooks with prenumbered pages, personnel qualification and training forms, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and analytical change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising laboratory records should be clearly defined, with the lines of authority included. Any documentation errors should be corrected by drawing a single line through the error so that it remains legible and should be initialed by the responsible individual, along with the date of change. The correction is written adjacent to the error.

Strip-chart recorder printouts should be signed by the person who performed the instrumental analysis. If corrections need to be made in computerized data, a system parallel to the corrections for handwritten data should be in place.

Records of sample management should be available to permit the re-creation of an analytical event for review in the case of an audit or investigation of a dubious result.

Laboratory records should include, at least, the following:

Operating Procedures -- Procedures should be available to those performing the task outlined. Any revisions to laboratory procedures should be written; dated, and distributed to all affected individuals to ensure implementation of changes. Areas covered by operating procedures are given in Sections 3.3 and 4.3.

Quality Assurance Plans -- The QAPjP should be on file.

Equipment Maintenance Documentation -- A history of the maintenance record of each system serves as an indication of the adequacy of maintenance schedules and parts inventory. As appropriate, the maintenance guidelines of the equipment manufacturer should be followed. When maintenance is necessary, it should be documented in either standard forms or in logbooks. Maintenance procedures should be clearly defined and written for each measurement system and required support equipment.

Proficiency -- Proficiency information on all compounds reported should be maintained and should include (1) precision; (2) bias; (3) method detection limits; (4) spike recovery, where applicable; (5) surrogate recovery, where applicable; (6) checks on reagent purity, where applicable; and (7) checks on glassware cleanliness, where applicable.

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include provisions for documenting frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy and traceability of all working standards against appropriate primary grade standards or the highest quality standards available should be routinely followed.

Sample Management -- All required records pertaining to sample management should be maintained and updated regularly. These include chain-of-custody forms, sample receipt forms, and sample disposition records.

Original Data -- The raw data and calculated results for all samples should be maintained in laboratory notebooks, logs, benchsheets, files or other sample tracking or data entry forms. Instrumental output should be stored in a computer file or a hardcopy report.

QC Data -- The raw data and calculated results for all QC and field samples and standards should be maintained in the manner described in the preceding paragraph. Documentation should allow correlation of sample results with associated QC data. Documentation should also include the source and lot numbers of standards for traceability. QC samples include, but are not limited to, control samples, method blanks, matrix spikes, and matrix spike duplicates.

Correspondence -- Project correspondence can provide evidence supporting technical interpretations. Correspondence pertinent to the project should be kept and placed in the project files.

Deviations -- All deviations from procedural and planning documents should be recorded in laboratory notebooks. Deviations from QAPjPs should be reviewed and approved by the authorized personnel who performed the original technical review or by their designees.

Final Report -- A copy of any report issued and any supporting documentation should be retained.

5.0 DEFINITIONS

The following terms are defined for use in this document:

ACCURACY — The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

BATCH: — A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit (see Section 3.4.1 for field samples and Section 4.4.3 for laboratory samples). For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BIAS: — The deviation due to matrix effects of the measured value ($x_s - x_u$) from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$$B = (x_s - x_u) - K$$

where:

x_s = measured value for spiked sample,
x_u = measured value for unspiked sample, and
K = known value of the spike in the sample.

Using the following equation yields the percent recovery (%R).

$$\%R = 100\ (x_s - x_u)/\ K$$

BLANK: see Equipment Rinsate, Method Blank, Trip Blank.

CONTROL SAMPLE: A QC sample introduced into a process to monitor the performance of the system.

DATA QUALITY OBJECTIVES (DQOs): A statement of the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data (see reference 2, EPA/QAMS, July 16, 1986). This is qualitatively distinct from quality measurements such as precision, bias, and detection limit.

DATA VALIDATION: The process of evaluating the available data against the project DQOs to make sure that the objectives are met. Data validation may be very rigorous, or cursory, depending on project DQOs. The available data reviewed will include analytical results, field QC data and lab QC data, and may also include field records.

DUPLICATE: see Matrix Duplicate, Field Duplicate, Matrix Spike Duplicate.

EQUIPMENT BLANK: see Equipment Rinsate.

EQUIPMENT RINSATE: A sample of analyte-free media which has been used to rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment.

ESTIMATED QUANTITATION LIMIT (EQL): The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected as the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs in SW-846 are provided for guidance and may not always be achievable.

FIELD DUPLICATES: Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

LABORATORY CONTROL SAMPLE: A known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.

MATRIX: The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.

MATRIX DUPLICATE: An intralaboratory split sample which is used to document the precision of a method in a given sample matrix.

MATRIX SPIKE: An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

METHOD BLANK: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank should be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern should not be higher than the highest of either:

(1)The method detection limit, or

(2)Five percent of the regulatory limit for that analyte, or

(3)Five percent of the measured concentration in the sample.

METHOD DETECTION LIMIT (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from

analysis of a sample in a given matrix type containing the analyte.

For operational purposes, when it is necessary to determine the MDL in the matrix, the MDL should be determined by multiplying the appropriate one-sided 99% t-statistic by the standard deviation obtained from a minimum of three analyses of a matrix spike containing the analyte of interest at a concentration three to five times the estimated MDL, where the t-statistic is obtained from standard references or the table below.

No. of samples:	t-statistic
3	6.96
4	4.54
5	3.75
6	3.36
7	3.14
8	3.00
9	2.90
10	2.82

Estimate the MDL as follows:
Obtain the concentration value that corresponds to:

a) an instrument signal/noise ratio within the range of 2.5 to 5.0, or

b) the region of the standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve).

Determine the variance (S^2) for each analyte as follows:

$$s^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} (x_i - \bar{x})^2\right]$$

where x_i = the ith measurement of the variable x
and $\bar{x}$ = the average value of x;

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

Determine the standard deviation (s) for each analyte as follows:

$$s = (S^2)^{1/2}$$

Determine the MDL for each analyte as follows:

$$MDL = t_{(n-1,\ \alpha = .99)}(s)$$

where $t_{(n-1,\ \alpha = .99)}$ is the one-sided t-statistic appropriate for the number of samples used to determine (s), at the 99 percent level.

ORGANIC-FREE REAGENT WATER:

For volatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water. Organic-free reagent water may also be prepared by boiling water for 15 minutes and, subsequently, while maintaining the temperature at 90°C, bubbling a contaminant-free inert gas through the water for 1 hour.

For semivolatiles and nonvolatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water.

PRECISION:

The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may involve the use of matrix spikes. The most commonly used estimates of precision are the relative standard deviation (RSD) or the coefficient of variation (CV),

$$RSD = CV = 100\ S/\bar{x},$$

where:
$\bar{x}$ = the arithmetic mean of the x_i measurements, and S = variance; and the relative percent difference (RPD) when only two samples are available.

$$RPD = 100\ [(x_1 - x_2)/((x_1 + x_2)/2)].$$

PROJECT: Single or multiple data collection activities that are related through the same planning sequence.

QUALITY ASSURANCE PROJECT PLAN (QAPjP): An orderly assemblage of detailed procedures designed to produce data of sufficient quality to meet the data quality objectives for a specific data collection activity.

RCRA: The Resource Conservation and Recovery Act.

REAGENT BLANK: See Method Blank.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

SPLIT SAMPLES: Aliquots of sample taken from the same container and analyzed independently. In cases where aliquots of samples are impossible to obtain, field duplicate samples should be taken for the matrix duplicate analysis. These are usually taken after mixing or compositing and are used to document intra- or interlaboratory precision.

STANDARD ADDITION: The practice of adding a known amount of an analyte to a sample immediately prior to analysis. It is typically used to evaluate interferences.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate

section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

SURROGATE: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.

TRIP BLANK: A sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

6.0 REFERENCES

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* Definition of term.

APPENDIX B2

ORGANIC ANALYTES

CHAPTER FOUR

ORGANIC ANALYTES

4.1 GENERAL CONSIDERATIONS

4.1.1 Introduction

Following the initial and critical step of designing a sampling plan (Chapter Nine) is the implementation of that plan such that a representative sample of the solid waste is collected. Once the sample has been collected it must be stored and preserved to maintain the chemical and physical properties that it possessed at the time of collection. The sample type, type of containers and their preparation, possible forms of contamination, and preservation methods are all items which must be thoroughly examined in order to maintain the integrity of the samples. This section highlights considerations which must be addressed in order to maintain a sample's integrity and representativeness. This section is, however, applicable only to trace analyses.

Quality Control requirements need not be met for all compounds presented in the Table of Analytes for the method in use, rather, they must be met for all compounds reported. A report of non-detect is considered a quantitative report, and must meet all applicable QC requirements for that compound and the method used.

4.1.2 Sample Handling and Preservation

This section deals separately with volatile and semivolatile organics. Refer to Chapter Two and Table 4-1 of this Section for recommended sample containers, sample preservation, and sample holding times.

Volatile Organics

Standard 40 mL glass screw-cap VOA vials with Teflon lined silicone septa may be used for both liquid and solid matrices. The vials and septa should be washed with soap and water and rinsed with distilled deionized water. After thoroughly cleaning the vials and septa, they should be placed in an oven and dried at 100 °C for approximately one hour.

NOTE: Do not heat the septa for extended periods of time (i.e. more than one hour, because the silicone begins to slowly degrade at 105°C).

When collecting the samples, liquids and solids should be introduced into the vials gently to reduce agitation which might drive off volatile compounds. Liquid samples should be poured into the vial without introducing any air bubbles within the vial as it is being filled. Should bubbling occur as a result of violent pouring, the sample must be poured out and the vial refilled. Each VOA vial should be filled until there is a meniscus over the lip of the vial. The screw-top lid with the septum (Teflon side toward the sample) should then be tightened onto the vial. After tightening the lid, the vial should be inverted and tapped to check for air bubbles. If there are any air bubbles present the sample must be recollected. Two VOA vials should be filled per sample location.

VOA vials for samples with solid or semi-solid matrices (e.g., sludges) should be completely filled as best as possible. The vials should be tapped slightly as they are filled to try and eliminate as much free air space as possible. Two vials should also be filled per sample location.

VOA vials should be filled and labeled immediately at the point at which the sample is collected. They should NOT be filled near a running motor or any type of exhaust system because discharged fumes and vapors may contaminate the samples. The two vials from each sampling location should then be sealed in separate plastic bags to prevent cross-contamination between samples, particularly if the sampled waste is suspected of containing high levels of volatile organics. (Activated carbon may also be included in the bags to prevent cross-contamination from highly contaminated samples). VOA samples may also be contaminated by diffusion of volatile organics through the septum during shipment and storage. To monitor possible contamination, a trip blank prepared from organic-free reagent water (as defined in Chapter One) should be carried throughout the sampling, storage, and shipping process.

Semivolatile Organics (including Pesticides, PCBs and Herbicides.)

Containers used to collect samples for the determination of semivolatile organic compounds should be soap and water washed followed by methanol (or isopropanol) rinsing (see Section 4.1.4 for specific instructions on glassware cleaning). The sample containers should be of glass or Teflon, and have screw-caps with Teflon lined septa. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. Highly acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples should not be collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g. if an automatic sampler is used), run organic-free reagent water through the sampler and use as a field blank.

4.1.3 Safety

Safety should always be the primary consideration in the collection of samples. A thorough understanding of the waste production process, as well as all of the potential hazards making up the waste, should be investigated whenever possible. The site should be visually evaluated just prior to sampling to determine additional safety measures. Minimum protection of gloves and safety glasses should be worn to prevent sample contact with the skin and eyes. A respirator should be worn even when working outdoors if organic vapors are present. More hazardous sampling missions may require the use of supplied air and special clothing.

4.1.4 Cleaning of Glassware

In the analysis of samples containing components in the parts per billion range, the preparation of scrupulously clean glassware is mandatory. Failure to do so can lead to a myriad of problems in the interpretation of the final chromatograms due to the presence of extraneous peaks resulting from

contamination. Particular care must be taken with glassware such as Soxhlet extractors, Kuderna-Danish evaporative concentrators, sampling-train components, or any other glassware coming in contact with an extract that will be evaporated to a smaller volume. The process of concentrating the compounds of interest in this operation may similarly concentrate the contaminating substance(s), which may seriously distort the results.

The basic cleaning steps are:

1. Removal of surface residuals immediately after use;

2. Hot soak to loosen and float most particulate material;

3. Hot water rinse to flush away floated particulates;

4. Soak with an oxidizing agent to destroy traces of organic compounds;

5. Hot water rinse to flush away materials loosened by the deep penetrant soak;

6. Distilled water rinse to remove metallic deposits from the tap water;

7. Alcohol, e.g., isopropanol or methanol, rinse to flush off any final traces of organic materials and remove the water; and

8. Flushing the item immediately before use with some of the same solvent that will be used in the analysis.

Each of these eight fundamental steps will be discussed in the order in which they appear above.

1. As soon possible after glassware (i.e. beakers, pipets, flasks, or bottles) has come in contact with sample or standards, the glassware should be flushed with alcohol before it is placed in the hot detergent soak. If this is not done, the soak bath may serve to contaminate all other glassware placed therein.

2. The hot soak consists of a bath of a suitable detergent in water of 50°C or higher. The detergent, powder or liquid, should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some hard-water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard-water scum or curd would have an affinity particularly for many chlorinated compounds and, being almost wholly water-insoluble, would deposit on all glassware in the bath in a thin film.

   There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form, is manufactured by Alconox, Inc., New York, and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

3. No comments required.

4. The most common and highly effective oxidizing agent for removal of traces of organic compounds is the traditional chromic acid solution made up of concentrated sulfuric acid and potassium or sodium dichromate. For maximum efficiency, the soak solution should be hot (40-50°C). Safety precautions must be rigidly observed in the handling of this solution. Prescribed safety gear should include safety goggles, rubber gloves. and apron. The bench area where this operation is conducted should be covered with fluorocarbon sheeting because spattering will disintegrate any unprotected surfaces.

   The potential hazards of using chromic sulfuric acid mixture are great and have been well publicized. There are now commercially available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca. 0.1 N NaOH upon dilution, and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attack glass or exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157," manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex," a product of Borer-Chemie, Solothurn, Switzerland.

5, 6, and 7. No comments required.

8. There is always a possibility that between the time of washing and the next use, the glassware could pick up some contamination from either the air or direct contact. To ensure against this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

The drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended . It is recommended that laboratory glassware and equipment be dried at 100 °C. Under no circumstances should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

As an alternate to solvent rinsing, the glassware can be heated to a minimum of 300 °C to vaporize any organics. Do not use this high temperature treatment on volumetric glassware, glassware with ground glass joints, or sintered glassware.

1.5 High Concentration Samples

Cross contamination of trace concentration samples may occur when prepared in the same laboratory with high concentration samples. Ideally, if both type samples are being handled, a laboratory and glassware dedicated solely to the preparation of high concentration samples would be available for this purpose. If this is not feasible, as a minimum when preparing high concentration samples, disposable glassware should be used or, at least, glassware dedicated entirely to the high concentration samples. Avoid cleaning glassware used for both trace and high concentration samples in the same area.

TABLE 4-1.
RECOMMENDED SAMPLE CONTAINERS, PRESERVATION
TECHNIQUES, AND HOLDING TIMES

Analyte Class	Container	Preservative	Holding Time
Volatile Organics			
Concentrated Waste Samples	8 oz. widemouth. glass with Teflon liner	None.	14 days
Liquid Samples			
No Residual Chlorine Present	2 X 40 mL vials with Teflon lined septum caps.	Cool, 4°C.[1]	14 days
Residual Chlorine Present	2 X 40 mL vials with Teflon lined septum caps.	Collect sample in a 4 oz. soil VOA container which has been pre-preserved with 4 drops of 10% sodium thiosulfate. Gently mix sample and transfer to a 40 mL VOA vial[1]. Cool to 4°C.	14 days
Acrolein and Acrylonitrile	2 X 40 mL vials with Teflon lined septum caps.	Adjust to pH 4-5, Cool, 4°C.	14 days
Soil/Sediments and Sludges	4 oz (120 mL) widemouth glass with Teflon liner, or wide mouth glass container sealed with a septum.	Cool, 4°C.	14 days

[1] Adjust pH <2 with H_2SO_4, HCl or solid $NaHSO_4$.

TABLE 4-1.
(Continued)

Analyte Class	Container	Preservative	Holding Time
Semivolatile Organics/Organochlorine Pesticides/PCBs and Herbicides			
Concentrated Waste Samples	8 oz. widemouth glass with Teflon liner	None	Samples must be extracted within 14 days and extracts analyzed within 40 days following extraction.
Water Samples			
No Residual Chlorine Present	1-gal. or 2 x 0.5-gal. amber glass with Teflon liner	Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction.
Residual Chlorine Present	1-gal. or 2 x 0.5-gal. amber glass with Teflon liner	Add 3 mL 10% sodium thiosulfate per gallon, Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction.
Soil/Sediments and Sludges	8 oz. widemouth glass with Teflon liner	Cool, 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days following extraction.

APPENDIX B3

GAS CHROMATOGRAPHY

METHOD 8000A

GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Gas chromatography is a quantitative technique useful for the analysis of organic compounds capable of being volatilized without being decomposed or chemically rearranged. Gas chromatography (GC), also known as vapor phase chromatography (VPC), has two subcategories distinguished by: gas-solid chromatography (GSC), and gas-liquid chromatography (GLC) or gas-liquid partition chromatography (GLPC). This last group is the most commonly used, distinguished by type of column adsorbent or packing.

1.2 The chromatographic methods are recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 SUMMARY OF METHOD

2.1 Each organic analytical method that follows provides a recommended technique for extraction, cleanup, and occasionally, derivatization of the samples to be analyzed. Before the prepared sample is introduced into the GC, a procedure for standardization must be followed to determine the recovery and the limits of detection for the analytes of interest. Following sample introduction into the GC, analysis proceeds with a comparison of sample values with standard values. Quantitative analysis is achieved through integration of peak area or measurement of peak height.

3.0 INTERFERENCES

3.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or of water to check for cross contamination. For volatile samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide concentrations, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak areas is recommended.

4.2 Gas chromatographic columns - See the specific determinative method. Other packed or capillary (open-tubular) columns may be used if the requirements

of Section 8.6 are met.

5.0 REAGENTS

5.1 See the specific determinative method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Extraction - Adhere to those procedures specified in the referring determinative method.

7.2 Cleanup and separation - Adhere to those procedures specified in the referring determinative method.

7.3 The recommended gas chromatographic columns and operating conditions for the instrument are specified in the referring determinative method.

7.4 Calibration

7.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.0 of the determinative method of interest. Prepare calibration standards using the procedures indicated in Section 5.0 of the determinative method of interest. Calibrate the chromatographic system using either the external standard technique (Section 7.4.2) or the internal standard technique (Section 7.4.3).

7.4.2 External standard calibration procedure

7.4.2.1 For each analyte of interest, prepare calibration standards at a minimum of five concentrations by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.2.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g. 2-5 μL injections, purge-and-trap, etc.). Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the

percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

$$\text{Calibration factor} = \frac{\text{Total Area of Peak}^{*}}{\text{Mass injected (in nanograms)}}$$

* For multiresponse pesticides/PCBs, use the total area of all peaks used for quantitation.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than ± 15%, a new calibration curve must be prepared for that analyte. For methods 8010, 8020, and 8030, see Table 3 in each method for calibration and quality control acceptance criteria.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration Factor from first analysis.

R_2 = Calibration Factor from succeeding analyses.

7.4.3 Internal standard calibration procedure

7.4.3.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.2 Prepare calibration standards at a minimum of five concentrations for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with an appropriate solvent. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.3.3 Inject each calibration standard using the same introduction technique that will be applied to the actual samples (e.g. 2 to 5 μL injection, purge-and-trap, etc.). Tabulate the peak height or area responses against the concentration of each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the analyte to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard, μg/L.

C_s = Concentration of the analyte to be measured, μg/L.

If the RF value over the working range is constant (< 20% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} versus RF.

7.4.3.4 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than ± 15%, a new calibration curve must be prepared for that compound. For methods 8010, 8020, and 8030, see Table 3 in each method for calibration and quality control acceptance criteria.

7.5 Retention time windows

7.5.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all single component standard mixtures and multiresponse products (i.e. PCBs) throughout the course of a 72 hour period. Serial injections over less than a 72 hour period result in retention time windows that are too tight.

7.5.2 Calculate the standard deviation of the three retention times (use any function of retention time; including absolute retention time, or relative retention time) for each single component standard. For multiresponse products, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

7.5.2.1 Plus or minus three times the standard deviation of the retention times for each standard will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse analytes (i.e. PCBs), the analyst should use the retention time window, but should primarily rely on pattern recognition.

7.5.2.2 In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

7.5.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.6 Gas chromatographic analysis

7.6.1 Introduction of organic compounds into the gas chromatograph varies depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap (Method 5030). However, there are limited applications (in Method 5030) where direct injection is acceptable. Use of Method 3810 or 3820 as a screening technique for volatile organic analysis may be valuable with some sample matrices to prevent overloading and contamination of the GC systems. Semivolatile organics are introduced by direct injection.

7.6.2 The appropriate detector(s) is given in the specific method.

7.6.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with multi-concentration calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.6.4 Direct Injection - Inject 2-5 μL of the sample extract using the solvent flush technique, if the extract is manually injected. Smaller volumes (1.0 μL) can be injected, and the solvent flush technique is not required, if automatic devices are employed. Record the volume injected to the nearest 0.05 μL and the resulting peak size in area units or peak height.

7.6.5 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.6.6 If peak detection is prevented by the presence of interferences, further cleanup is required.

7.6.7 Examples of chromatograms for the compounds of interest are frequently available in the referring analytical method.

7.6.8 Calibrate the system immediately prior to conducting any analyses (see Section 7.4). A mid-concentration standard must also be injected at intervals specified in the method and at the end of the analysis sequence. The calibration factor for each analyte to be quantitated, must not exceed a 15% difference when compared to the initial standard of the analysis sequence. When this criterion is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary (see Section 7.7) before recalibrating and proceeding with sample analysis. All samples that were injected after the standard exceeding the criterion must be reinjected to avoid errors in quantitation, if the initial analysis indicated the presence of the specific target analytes that exceeded the criterion.

7.6.9 Establish daily retention time windows for each analyte. Use the retention time for each analyte from Section 7.6.8 as the midpoint of the window for that day. The daily retention time window equals the midpoint $\pm$ three times the standard deviation determined in Section 7.5.

7.6.9.1 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Normally, confirmation is required: on a second GC column, by GC/MS if concentration permits, or by other recognized confirmation techniques. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.

7.6.9.2 Validation of GC system qualitative performance: Use the mid-concentration standards interspersed throughout the analysis sequence (Section 7.6.8) to evaluate this criterion. If any of the standards fall outside their daily retention time window, the system is out of control. Determine the cause of the problem and correct it (see Section 7.7). All samples that were injected after the standard exceeding the criteria must be reinjected to avoid false negatives and possibly false positives.

7.7 Suggested chromatography system maintenance - Corrective measures may require any one or more of the following remedial actions.

7.7.1 Packed columns - For instruments with injection port traps, replace the demister trap, clean, and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Inspect the injection end of the column and remove any foreign material (broken glass from the rim of the column or pieces of septa). Replace the glass wool with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of the packing material if any discoloration is noted, also swab out the inside walls of the column if any residue is noted. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described in Section 7.7.3) and/or repack/replace the column.

7.7.2 Capillary columns - Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Break off the first few inches, up to one foot, of the injection port side of the column. Remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

7.7.3 Metal injector body - Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.7.3.1 Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene; catching the rinsate in the beaker.

7.7.3.2 Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the GC column.

7.8 Calculations

7.8.1 External standard calibration - The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the calibration curve or the calibration factor determined in Section 7.4.2. The concentration of a specific analyte is calculated as follows:

Aqueous samples

$$\text{Concentration } (\mu g/L) = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(V_s)]$$

where:

A_x = Response for the analyte in the sample, units may be in area counts or peak height.

A = Amount of standard injected or purged, ng.

A_s = Response for the external standard, units same as for A_x.

V_i = Volume of extract injected, μL. For purge-and-trap analysis, V_i is not applicable and therefore = 1.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

V_t = Volume of total extract, μL. For purge-and-trap analysis, V_t is not applicable and therefore = 1.

V_s = Volume of sample extracted or purged, mL.

Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = [(A_x)(A)(V_t)(D)]/[(A_s)(V_i)(W)]$$

where:

W = Weight of sample extracted or purged, g. The wet weight or dry weight may be used, depending upon the specific applications of the data.

A_x, A_s, A, V_t, D, and V_i have the same definition as for aqueous samples when a solid sample is purged (e.g., low concentration soil) for volatile organic analysis or for semivolatile organic and pesticide extracts. When the nonaqueous sample is extracted for purge and trap analysis, V_i = volume of methanol extract added to reagent water for purge and trap analysis.

7.8.2 Internal standard calibration - For each analyte of interest, the concentration of that analyte in the sample is calculated as follows:

Aqueous samples

$$\text{Concentration } (\mu g/L) = [(A_x)(C_{is})(D)]/[(A_{is})(RF)(V_s)]$$

where:

A_x = Response of the analyte being measured, units may be in area counts or peak height.

C_{is} = Amount of internal standard added to extract or volume purged, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x.

RF = Response factor for analyte, as determined in Section 7.4.3.3.

V_s = Volume of water extracted or purged, mL.

Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = [(A_s)(C_{is})(D)]/[(A_{is})(RF)(W_s)]$$

where:

W_s = Weight of sample extracted, g. Either a dry weight or wet weight may be used, depending upon the specific application of the data.

A_s, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory should maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard should be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, an organic-free reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike, and duplicate or matrix spike duplicate should be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples should be carried through all stages of the sample preparation and measurement steps.

8.4 The experience of the analyst performing gas chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system should take place.

8.5 Required instrument QC

8.5.1 Step 7.4 requires that the %RSD vary by < 20% when comparing calibration factors to determine if a five point calibration curve is linear.

8.5.2 Section 7.4 sets a limit of ± 15% difference when comparing daily response of a given analyte versus the initial response. For Methods 8010, 8020, and 8030, follow the guidance on limits specified in Section 7.4.3.4. If the limit is exceeded, a new standard curve should be prepared unless instrument maintenance corrects the problem for that particular analyte.

8.5.3 Step 7.5 requires the establishment of retention time windows.

8.5.4 Section 7.6.8 sets a limit of ± 15% difference when comparing the response from the continuing calibration standard of a given analyte versus any succeeding standards analyzed during an analysis sequence.

8.5.5 Step 7.6.9.2 requires that all succeeding standards in an analysis sequence should fall within the daily retention time window established by the first standard of the sequence.

8.6 To establish the ability to generate acceptable accuracy and precision, the analyst should perform the following operations.

8.6.1 A quality control (QC) check sample concentrate is required containing each analyte of interest. The QC check sample concentrate may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate should be made using stock standards prepared independently from those used for calibration.

8.6.1.1 The concentration of the QC check sample concentrate is highly dependent upon the analytes being investigated. Therefore, refer to Method 3500, Section 8.0 for the required concentration of the QC check sample concentrate.

8.6.2 Preparation of QC check samples

8.6.2.1 Volatile organic analytes (Methods 8010, 8020, and 8030) - The QC check sample is prepared by adding 200 µL of the QC check sample concentrate (Step 8.6.1) to 100 mL of water.

8.6.2.2 Semivolatile organic analytes (Methods 8040, 8060, 8070, 8080, 8090, 8100, 8110, and 8120) - The QC check sample is prepared by adding 1.0 mL of the QC check sample concentrate (Step 8.6.1) to each of four 1-L aliquots of water.

8.6.3 Four aliquots of the well-mixed QC check sample are analyzed by the same procedures used to analyze actual samples (Section 7.0 of each of the methods). For volatile organics, the preparation/analysis process is purge-and-trap/gas chromatography. For semivolatile organics, the QC check samples should undergo solvent extraction (see Method 3500) prior to chromatographic analysis.

8.6.4 Calculate the average recovery ($\bar{x}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each analyte of interest using the four results.

8.6.5 For each analyte compare s and $\bar{x}$ with the corresponding acceptance criteria for precision and accuracy, respectively, given the QC Acceptance Criteria Table at the end of each of the determinative methods. If s and $\bar{x}$ for all analytes of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{x}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in each of the QC Acceptance Criteria Tables present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.6.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst should proceed according to Step 8.6.6.1 or 8.6.6.2.

8.6.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Step 8.6.2.

8.6.6.2 Beginning with Step 8.6.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Step 8.6.2.

8.7 The laboratory should, on an ongoing basis, analyze a reagent blank and a matrix spiked duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of spiked duplicates. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.7.1 The concentration of the spike in the sample should be determined as follows:

8.7.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit, or 1 to 5 times higher than the background concentration determined in Step 8.7.2, whichever concentration would be larger.

8.7.1.2 If the concentration of a specific analyte in a water sample is not being checked against a limit specific to that analyte, the spike should be at the same concentration as the QC reference sample (Step 8.6.2) or 1 to 5 times higher than the background concentration determined in Step 8.7.2, whichever concentration would be larger. For other matrices, the recommended spiking concentration is 20 times the EQL.

8.7.1.3 For semivolatile organics, it may not be possible to determine the background concentration levels prior to spiking (e.g. maximum holding times will be exceeded). If this is the case, the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the QC reference sample concentration (Step 8.6.2). For other matrices, the recommended spiking concentration is 20 times the EQL.

8.7.2 Analyze one unspiked and one spiked sample aliquot to determine percent recovery of each of the spiked compounds.

8.7.2.1 Volatile organics - Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.6.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 μL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A - B)%/T, where T is the known true value of the spike.

8.7.2.2 Semivolatile organics - Analyze one sample aliquot (extract of 1-L sample) to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.6.1) appropriate for the background concentration in the sample. Spike a second 1-L sample aliquot with 1.0 mL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as 100(A - B)%/T, where T is the known true value of the spike.

8.7.3 Compare the percent recovery (p) for each analyte in a water sample with the corresponding criteria presented in the QC Acceptance Criteria Table found at the end of each of the determinative methods. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than the QC reference sample concentration (Step 8.6.2), the analyst should use either the QC acceptance criteria presented in the Tables, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in the Method Accuracy and Precision as a Function of Concentration Table (appears at the end of each determinative method), substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in the same Table, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.7.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria should be

analyzed as described in Step 8.8.

8.8 If any analyte in a water sample fails the acceptance criteria for recovery in Step 8.7, a QC reference standard containing each analyte that failed should be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC reference standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes given in a method should be measured in the sample in Step 8.7, the probability that the analysis of a QC check standard will be required is high. In this case, the QC check standard should be routinely analyzed with the spiked sample.

8.8.1 Preparation of the QC check sample - For volatile organics, add 10 µL of the QC check sample concentrate (Step 8.6.1 or 8.7.2) to 5 mL of water. For semivolatile organics, add 1.0 mL of the QC check sample concentrate (Step 8.6.1 or 8.7.2) to 1 L of water. The QC check sample needs only to contain the analytes that failed criteria in the test in Step 8.7. Prepare the QC check sample for analysis following the guidelines given in Method 3500 (e.g. purge-and-trap, extraction, etc.).

8.8.2 Analyze the QC check sample to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100(A/T)%, where T is the true value of the standard concentration.

8.8.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in the appropriate Table in each of the methods. Only analytes that failed the test in Step 8.7 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem should be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.9 As part of the QC program for the laboratory, method accuracy for each matrix studied should be assessed and records should be maintained. After the analysis of five spiked samples (of the same matrix type) as in Step 8.7, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.10 Calculate surrogate control limits as follows:

8.10.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.10.2 Calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates when

surrogate data from 25 to 30 samples for each matrix is available.

8.10.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

8.10.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits in Tables A and B of Methods 8240 and 8270, respectively. The limits given in these methods are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.10.3 should fall within those given in Tables A and B for these matrices.

8.10.5 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.10.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.11 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer should be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

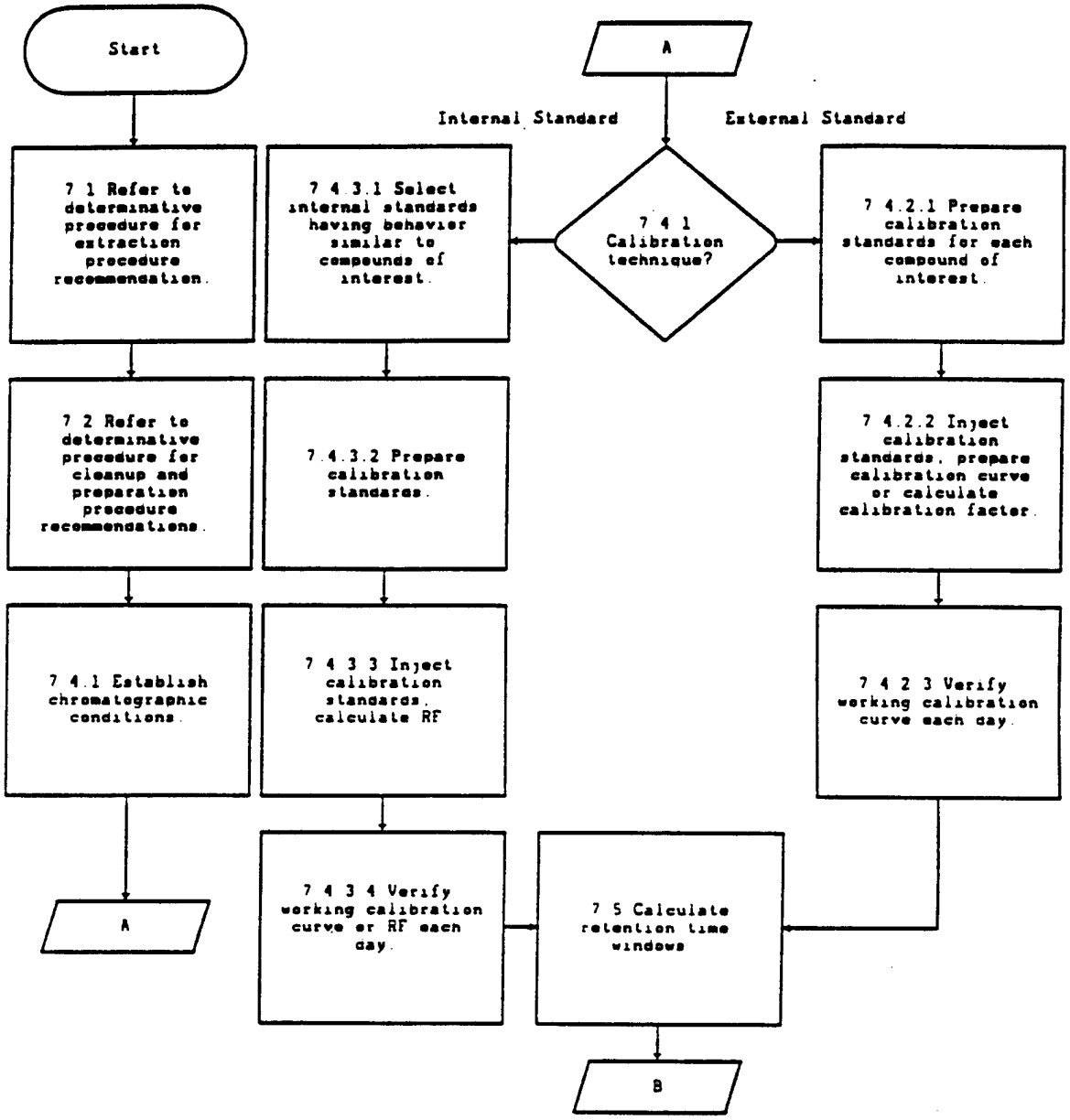
9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in the referring analytical methods were obtained using water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

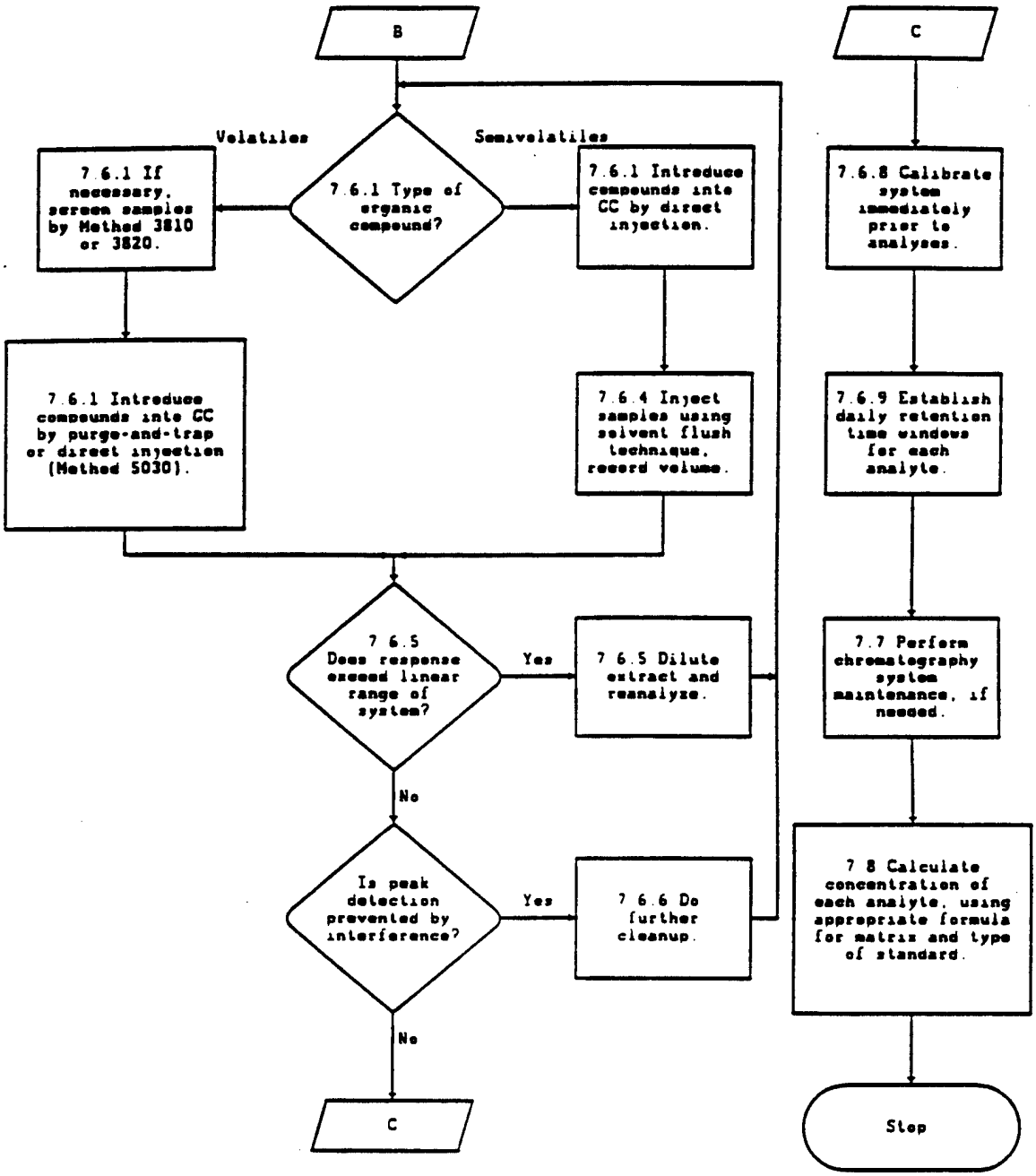
9.2 Refer to the determinative method for specific method performance information.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.


Start
A
Internal Standard
External Standard
7 1 Refer to determinative procedure for extraction procedure recommendation.
7 4.3.1 Select internal standards having behavior similar to compounds of interest.
7 4 1 Calibration technique?
7 4.2.1 Prepare calibration standards for each compound of interest.
7 2 Refer to determinative procedure for cleanup and preparation procedure recommendations.
7.4.3.2 Prepare calibration standards.
7 4.2.2 Inject calibration standards, prepare calibration curve or calculate calibration factor.
7 4.1 Establish chromatographic conditions.
7 4 3 3 Inject calibration standards, calculate RF
7 4 2 3 Verify working calibration curve each day.
A
7 4 3 4 Verify working calibration curve or RF each day.
7 5 Calculate retention time windows
B


B
C
Volatiles
Semivolatiles
7.6.1 If necessary, screen samples by Method 3810 or 3820.
7.6.1 Type of organic compound?
7.6.1 Introduce compounds into GC by direct injection.
7.6.8 Calibrate system immediately prior to analyses.
7.6.1 Introduce compounds into GC by purge-and-trap or direct injection (Method 5030).
7.6.4 Inject samples using solvent flush technique, record volume.
7.6.9 Establish daily retention time windows for each analyte.
7.6.5 Does response exceed linear range of system?
Yes
7.6.5 Dilute extract and reanalyze.
7.7 Perform chromatography system maintenance, if needed.
No
Is peak detection prevented by interference?
Yes
7.6.6 Do further cleanup.
7.8 Calculate concentration of each analyte, using appropriate formula for matrix and type of standard.
No
C
Stop

APPENDIX B4

METHOD 8330

EXPLOSIVES ANALYSIS

TENNESSEE VALLEY AUTHORITY

NO.: Method 8330

TITLE: NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMOTOGRAPHY (HPLC)

Signature	Title	Date
Prepared by: William J. Rogers	QA Officer	5/25/94
Concurred: Kathleen C. Pugh	Analytical Chemist	7/19/94
Concurred:		
Concurred:		
Concurred:		
Concurred:		
Approved: Joe J. Hoagland	Team Leader Specialist Analytical Laboratory	7/14/94

REVISION	R0			
CONTROL DATE:				

COPY NO.: _____ HAS BEEN ISSUED TO HOLDER ON _____

TVA 17207 (OPM-8-83)

Addendum to Method 8330

This Addendum serves to describe our interpretation of certain portions of Method 8330 and to describe curve fitting as actually performed.

1. Interpretation: Midpoint calibration standards are run in triplicate at the start of the run and every ten samples thereafter (and as the last sample of the run). These are counted **as they are loaded on the machine**. A pair of reagent blanks are usually run before the three initial midpoint calibration standards. For every twenty customer samples, one is selected to have an aliquot run with a matrix spike added and another aliquot run with a matrix spike duplicate. In addition, for every twenty customer samples, a method blank is run. Thus, an analytical run can be summarized as follows:

i	Reagent Blank
ii	Reagent Blank
iii	Midpoint Cal. Std.
iv	Midpoint Cal. Std.
v	Midpoint Cal. Std.
1	Method Blank
2	Laboratory Control Sample
3	Customer Sample 1
4	Customer Sample 2
5	Customer Sample 3
6	Customer Sample 4
7	Customer Sample 5
8	Matrix Spike of Sample 5
9	Matrix Spike Duplicate of 5
10	Customer Sample 6
	Midpoint Cal. Std.
11	Customer Sample 7
12	Customer Sample 8
13	Customer Sample 9
14	Customer Sample 10
15	Customer Sample 11
16	Customer Sample 12
17	Customer Sample 13
18	Customer Sample 14
19	Customer Sample 15
20	Customer Sample 16
	Midpoint Cal. Std.
21	Customer Sample 17
22	Customer Sample 18
23	Customer Sample 19
24	Customer Sample 20
25	Method Blank
26	Laboratory Control Sample
27	Customer Sample 21
28	Matrix Spike of 21
29	Matrix Spike Duplicate of 21
30	Customer Sample 22
	Midpoint Cal. Std.
31	Customer Sample 23
32	Customer Sample 24
etc.	

Here, "Reagent Blank" refers to only the solvents such as are used to make calibration solutions. "Method Blank" would include solvent or clean dry cloth smear carried through any preparation steps associated with the batch. The "Laboratory Control Sample" is called by other names in various documents. It is made using standard material other than that used in calibrating the machine. Note also that the customer sample to be spiked as the matrix spike and matrix spike duplicate may be chosen at random through any group of 20.

2. Modification: If any midpoint calibration standard does not fall within 15% of the daily average of the first three midpoint calibration standards, then the previous ten samples will be reanalysed.

3. Interpretation: Calibration curves will be run and utilized as described in Method 8330. Curves will be run based on peak height rather than peak area. Curve fits will be forced through the origin utilizing standard peak fitting software provided by the manufacturer of the chromatography system or a commercially available spreadsheet.

4. Interpretation: Calibration curves will be run initially. These curves will be placed into use and will be used until there is indication of a change in system response. They will not be re-run unless the midpoint calibration checks indicate that the response slope of the system has changed significantly. That is, there is no need to re-run the curves monthly or on any other frequency unless there is indication of a change. Furthermore, the solutions are being used longer than 30 days. Since they can be compared to their initial concentration, we intend to keep them in use until a change is indicated.

5. Modification: The calcium chloride in Step 5.5 "Working Standards" will be replaced with HPLC grade water. (The calcium chloride solution is present to coagulate clay particles in soil analysis.)

6. Modification: We will not be utilizing the dual-column confirmation analysis mentioned in steps 2.3, 4.1.2.2, 7.2, and 7.4.1. We know from the test plan what compounds should be present. We are not attempting to determine and confirm environmental pollutants.

7. Modification: We are not using surrogates as mentioned in step 5.6 at the request of the customer.

8. Modification: Our spiking solutions are in acetonitrile, not methanol as mentioned in 5.7.

9. Modification: We are not premixing the mobile phase as specified in step 5.8.1 but are mixing the reagents in the pump.

Method 8330
Appendix B - Sample Preparation

1.0 Sample Types

1.1 Samples received were one of three types:

1.1.1 Liquids (projectile extracts, impinger solutions or Tenax holder/impinger washings.)

1.1.2 Gauze smears (smear samples were taken from mine bodies which did not lend themselves to free liquid extraction or from the inside of the HGD chamber.)

1.1.3 Solids (Tenax resin, insulation, any other solids.)

2.0 Before sample preparation starts, place all samples in a dark area and allow them to reach room temperature.

3.0 Liquid Sample Preparation

Liquid samples are one of three matrices: acetonitrile (AcCN), water, or AcCN/hexane (used for extraction of Compound A). Each matrix is prepared for filtration differently:

3.1 Combine acetonitrile matrices 1:1 with water (usually 2 mL of sample plus 2 mL of water) in an 8 mL vial. Cap the vial and cover it with an aluminum foil sleeve. Shake it briefly and then place it in a dark area for a minimum of 20 minutes.

3.2 Combine water matrices, excluding those containing ammonium picrate, 1:1 with acetonitrile (usually 2 mL of sample plus 2 mL of acetonitrile) in an 8 mL vial . Cap the vial and cover it with an aluminum foil sleeve. Shake it briefly and then place it in a dark area for a minimum of 20 minutes.

3.3 For acetonitrile/hexane matrices, first remove as much of the hexane layer (top) as possible with a Pasteur pipette. Then combine the acetonitrile layer 1:1 with HPLC grade water (usually 2 mL of sample plus 2 mL of water) in an 8 mL vial . Cap the vial and cover it with an aluminum foil sleeve. Shake it briefly and then place it in a dark area for a minimum of 20 minutes. Before filtration, remove any hexane that had been forced out of the acetonitrile fraction by the water with a Pasteur pipette.

4.0 Smear Sample Preparation

4.1 Samples are received either in 100 or 250 mL size clear, pre-cleaned, wide-mouth bottles with Teflon-lined closures.

4.2 If the smear is contained in a 250 mL bottle, wrap the bottle with aluminum foil. Add 100 mL of acetonitrile (measured with a graduated cylinder) to the bottle along with a stir bar. Reseal the top.

4.3 If the smear is in a 100 mL bottle, transfer the smear to a new 250 mL bottle wrapped with aluminum foil. Use 100 mL of acetonitrile to rinse the 100 mL bottle into the new bottle. Add a stir bar to the new bottle and reseal the top.

4.4 Place the extraction bottles on a magnetic stirrer on medium speed for at least 1 hour.

4.5 Turn off the stirrers and allow the extractant solutions to settle for a short period of time.

4.6 Combine the acetonitrile extract 1:1 with HPLC grade water (usually 2 mL of sample plus 2 mL of water) in an 8 mL vial. Cap the vial and cover it with an aluminum foil sleeve. Shake it briefly and then place it in a dark area for a minimum of 20 minutes.

5.0 Solid Sample Preparation

5. Tenax

5.1.1 Samples of Tenax resin are usually received in glass Tenax resin sampling tubes which were sealed at both ends with Parafilm© and wrapped with aluminum foil.

5.1.2 Place the contents of the sampling tube in a 250 mL pre-cleaned bottle along with a stir bar.

5.1.3 Wrap the bottle with aluminum foil. Add 100 mL of acetonitrile by passing it through the inside bore of the resin sampling tube. Reseal the bottle.

5.2 Other solids

5.2.1 Other solids, such as insulation, are received in either 100 or 250 mL size bottles.

5.2.2 Remove the solids from their containers. Place them on a weighing boat. Weigh them on an analytical balance. Record the weight.

5.2.3 Transfer the solids to a new 250 mL pre-cleaned bottle which has been wrapped in aluminum foil. Add a stir bar to the bottle.

5.2.4 Add 100 mL of acetonitrile (portions of which were used to rinse the original sample container and the weighing boat) and reseal the bottle.

5.2.5 Place the extraction bottle on a magnetic stirrer on medium speed for at least 1 hour.

5.2.6 Turn the stirrers off and allow the extractant solutions to settle for a short period of time.

5.2.7 Combine the acetonitrile extract 1:1 with HPLC grade water (usually 2 mL of sample plus 2 mL of water) in an 8 mL vial. Cap the vial and cover it with an aluminum foil sleeve. Shake it briefly, and then place it in a dark area for a minimum of 20 minutes.

6.0 Filtration

6.1 At this point, the extracts from all three sample types (liquids, smears, and solids) are treated the same.

6.2 Pour the contents of each 8 mL vial into a 10 mL syringe whose plunger has been removed and to which is attached a 25 mm syringe filter.

6.3 Remount the syringe plunger and filter approximately 2 mL of solution into a waste breaker.

6.4 Filter a portion of the remaining solution into an amber autosampler vial.

6.5 Keep the autosampler vials in a dark area until they are loaded on the Varian model 9100 autosampler.

Method 8330
Appendix C - Quality Control

1.0 Field QC

Sample sets received from the Hawthorne test site contain a set of field quality control samples for every 20 samples consisting of a blank solution, spiked projectile sacrifice, high field QC solution, and low field QC solution. A sample of the stock solution used to make the high and low field QC spikes should also be present. Count these the same as other field samples in determining batch size.

2.0 Laboratory QC

Once in the laboratory, add the following list of quality control sample types for every 20 analytical samples: method blank, laboratory control sample, matrix spike, and matrix spike duplicate.

3.0 Method Blank

3.1 For liquid samples, use a 10 mL portion of acetonitrile treated as a normal analytical liquid sample.

3.2 For smears, place a clean gauze wipe in a pre-cleaned 250 mL jar along with a stir bar and 100 mL o acetonitrile.

3.3 Treat the sample as a normal analytical sample.

4.0 Laboratory Control Sample

4.1 The spike solution must be prepared from a source separate from that used for calibration standards. Match the spike solution to the analytes being studied (TNT, RDX, or both TNT and RDX). The spiking solution concentration should be made up to approximately 10 ug/mL for each analyte.

4.2 For liquid samples, add 0.5 mL of spike solution to a 10 mL volumetric flask. Bring it to volume with acetonitrile.

4.3 For smears, place a clean gauze wipe in a precleaned 250 mL jar along with a stir bar. Pipette 5 mL of spike solution onto the gauze wipe. Add 95mL of acetonitrile measured in a graduated cylinder.

4.4 Treat the sample as a normal analytical sample.

5.0 Matrix Spike and Matrix Spike Duplicate

5.1 Select a routine field sample (not a field QC sample, sacrifice or stock solution) at random to be spiked.

5.2 Match the spiking solution to the analytes being studied (TNT, RDX or both TNT and RDX). The spiking solution should be made up to approximately 10 ug/mL for each analyte.

5.3 Add 0.5 mL of spiking solution to a 10 mL volumetric flask. Bring it to volume with the liquid portion of a sample or the extract of a smear or solid sample.

5.4 Treat the sample as a normal analytical sample.

6.0 Control Charts

6.1 After samples are calculated, plot the following items on control charts:

6.1.1 Percent recovery of TNT or RDX for laboratory control samples.

6.1.2 Percent recovery for matrix spikes and matrix spike duplicates.

6.1.3 Initial calibration verification and continuing calibration verifications. Note: These are plotted on the same chart.

METHOD 8330

NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 Method 8330 is intended for the trace analysis of explosives residues by high performance liquid chromatography using a UV detector. This method is used to determine the concentration of the following compounds in a water, soil, or sediment matrix:

Compound	Abbreviation	CAS No[a]
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4
1,3-Dinitrobenzene	1,3-DNB	99-65-0
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	2,4,6-TNT	118-96-7
4-Amino-2,6-dinitrotoluene	4-Am-DNT	1946-51-0
2-Amino-4, 6-dinitrotoluene	2-Am-DNT	355-72-78-2
2,4-Dinitrotoluene	2,4-DNT	121-14-2
2,6-Dinitrotoluene	2,6-DNT	606-20-2
2-Nitrotoluene	2-NT	88-72-2
3-Nitrotoluene	3-NT	99-08-1
4-Nitrotoluene	4-NT	99-99-0

a Chemical Abstracts Service Registry number

1.2 Method 8330 provides a salting-out extraction procedure for low concentration (parts per trillion or nanograms per liter) of explosives residues in surface or ground water. Direct injection of diluted and filtered water samples can be used for water samples of higher concentration (See Table 1).

1.3 All of these compounds are either used in the manufacture of explosives or are the degradation products of compounds used for that purpose. When making stock solutions for calibration, treat each explosive compound with caution. See NOTE in Section 5.3.1 and Section 11 on Safety.

1.4 The estimated quantitation limits (EQLs) of target analytes determined by Method 8330 in water and soil are presented in Table 1.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC, skilled in the interpretation of chromatograms, and experienced in handling explosive materials. (See Section 11.0 on SAFETY.) Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Method 8330 provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain explosives residues in water, soil and sediment matrix. Prior to use of this method, appropriate sample preparation techniques must be used.

2.2 Low-Level Salting-out Method With No Evaporation: Aqueous samples of low concentration are extracted by a salting-out extraction procedure with acetonitrile and sodium chloride. The small volume of acetonitrile that remains undissolved above the salt water is drawn off and transferred to a smaller volumetric flask. It is back-extracted by vigorous stirring with a specific volume of salt water. After equilibration, the phases are allowed to separate and the small volume of acetonitrile residing in the narrow neck of the volumetric flask is removed using a Pasteur pipet. The concentrated extract is diluted 1:1 with reagent grade water. An aliquot is separated on a C-18 reverse phase column, determined at 254 nm, and confirmed on a CN reverse phase column.

2.3 High-level Direct Injection Method: Aqueous samples of higher concentration can be diluted 1/1 (v/v) with methanol or acetonitrile, filtered, separated on a C-18 reverse phase column, determine at 254 nm, and confirmed on a CN reverse phase column. If HMX is an important target analyte, methanol is preferred.

2.4 Soil and sediment samples are extracted using acetonitrile in an ultrasonic bath, filtered and chromatographed as in Section 2.3.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences.

3.2 2,4-DNT and 2,6-DNT elute at similar retention times (retention time difference of 0.2 minutes). A large concentration of one isomer may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.

3.3 Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain tetryl should be diluted with acetonitrile prior to filtration. All samples expected to contain tetryl should not be exposed to temperatures above room temperature.

3.4 Degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-TNT.

4.0 APPARATUS AND MATERIALS

4.1 HPLC system

4.1.1 HPLC - equipped with a pump capable of achieving 4000 psi, a 100 µl loop injector and a 254 nm UV detector (Perkin Elmer Series 3, or equivalent). For the low concentration option, the detector must be capable of a stable baseline at 0.001 absorbance units full scale.

4.1.2 Recommended Columns:

4.1.2.1 Primary column: C-18 Reverse phase HPLC column, 25 cm x 4.6 mm (5 µm), (Supelco LC-18, or equivalent).

4.1.2.2 Secondary column: CN Reverse phase HPLC column, 25 cm x 4.6 mm (5 µm), (Supelco LC-CN, or equivalent).

4.1.3 Strip chart recorder.

4.1.4 Digital integrator (optional).

4.1.5 Autosampler (optional).

4.2 Other Equipment

4.2.1 Temperature controlled ultrasonic bath.

4.2.2 Vortex mixer.

4.2.3 Balance ± 0.0001 g.

4.2.4 Magnetic stirrer with stirring pellets.

4.2.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.2.6 Oven - Forced air, without heating.

4.3 Materials

4.3.1 High pressure injection syringe - 500 µL, (Hamilton liquid syringe or equivalent).

4.3.2 Disposable cartridge filters - 0.45 µm Teflon filter.

4.3.3 Pipets - Class A, glass, Appropriate sizes.

4.3.4 Pasteur pipets.

4.3.5 Scintillation Vials - 20 mL, glass.

4.3.6 Vials - 15 mL, glass, Teflon-lined cap.

4.3.7 Vials- 40 mL, glass, Teflon-lined cap.

4.3.8 Disposable syringes - Plastipak, 3 mL and 10 mL or equivalent.

4.3.9 Volumetric flasks - Appropriate sizes with ground glass stoppers, Class A.

NOTE: The 100 mL and 1 L volumetric flasks used for magnetic stirrer extraction must be round.

4.3.10 Vacuum desiccator - Glass.

4.3.11 Mortar and pestle - Steel.

4.3.12 Sieve - 30 mesh.

4.3.13 Graduated cylinders - Appropriate sizes.

4.4 Preparation of Materials

4.4.1 Prepare all materials to be used as described in Chapter 4 for semivolatile organics.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination.

5.1.1 Acetonitrile, CH_3CN - HPLC grade.

5.1.2 Methanol, CH_3OH - HPLC grade.

5.1.3 Calcium chloride, $CaCl_2$ - Reagent grade. Prepare an aqueous solution of 5 g/L.

5.1.4 Sodium chloride, NaCl, shipped in glass bottles - reagent grade.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Stock Standard Solutions

5.3.1 Dry each solid analyte standard to constant weight in a vacuum desiccator in the dark. Place about 0.100 g (weighed to 0.0001 g) of a single analyte into a 100 mL volumetric flask and dilute to volume with acetonitrile. Invert flask several times until dissolved. Store in refrigerator at 4°C in the dark. Calculate the concentration of the stock

solution from the actual weight used (nominal concentration = 1,000 mg/L). Stock solutions may be used for up to one year.

NOTE: The HMX, RDX, Tetryl, and 2,4,6-TNT are explosives and the neat material should be handled carefully. See SAFETY in Section 11 for guidance. HMX, RDX, and Tetryl reference materials are shipped under water. Drying at ambient temperature requires several days. DO NOT DRY AT HEATED TEMPERATURES!

5.4 Intermediate Standards Solutions

5.4.1 If both 2,4-DNT and 2,6-DNT are to be determined, prepare two separate intermediate stock solutions containing (1) HMX, RDX, 1,3,5-TNB, 1,3-DNB, NB, 2,4,6-TNT, and 2,4-DNT and (2) Tetryl, 2,6-DNT, 2-NT, 3-NT, and 4-NT. Intermediate stock standard solutions should be prepared at 1,000 µg/L, in acetonitrile when analyzing soil samples, and in methanol when analyzing aqueous samples.

5.4.2 Dilute the two concentrated intermediate stock solutions, with the appropriate solvent, to prepare intermediate standard solutions that cover the range of 2.5 - 1,000 µg/L. These solutions should be refrigerated on preparation, and may be used for 30 days.

5.4.3 For the low-level method, the analyst must conduct a detection limit study and devise dilution series appropriate to the desired range. Standards for the low level method must be prepared immediately prior to use.

5.5 Working standards

5.5.1 Calibration standards at a minimum of five concentration levels should be prepared through dilution of the intermediate standards solutions by 50% (v/v) with 5 g/L calcium chloride solution (Section 5.1.3). These solutions must be refrigerated and stored in the dark, and prepared fresh on the day of calibration.

5.6 Surrogate Spiking Solution

5.6.1 The analyst should monitor the performance of the extraction and analytical system as well as the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and reagent water blank with one or two surrogates (e.g., analytes not expected to be present in the sample).

5.7 Matrix Spiking Solutions

5.7.1 Prepare matrix spiking solutions in methanol such that the concentration in the sample is five times the Estimated Quantitation Limit (Table 1). All target analytes should be included.

5.8 HPLC Mobile Phase

5.8.1 To prepare 1 liter of mobile phase, add 500 mL of methanol to 500 mL of organic-free reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Follow conventional sampling and sample handling procedures as specified for semivolatile organics in Chapt. 4.

6.2 Samples and sample extracts must be stored in the dark at 4°C. Holding times are the same as for semivolatile organics.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Aqueous Samples: It is highly recommended that process waste samples be screened with the high-level method to determine if the low level method (1-50 µg/L) is required. Most groundwater samples will fall into the low level method.

7.1.1.1 Low-Level Method (salting-out extraction)

7.1.1.1.1 Add 251.3 g of sodium sulfate to a 1 L volumetric flask (round). Measure out 770 mL of a water sample (using a 1 L graduated cylinder) and transfer it to the volumetric flask containing the salt. Add a stir bar and mix the contents at maximum speed on a magnetic stirrer until the salt is completely dissolved.

7.1.1.1.2 Add 164 mL of acetonitrile (measured with a 250 mL graduated cylinder) while the solution is being stirred and stir for an additional 15 minutes. Turn off the stirrer and allow the phases to separate for 10 minutes.

7.1.1.1.3 Remove the acetonitrile (upper) layer (about 8 mL) with a Pasteur pipet and transfer it to a 100 mL volumetric flask (round). Add 10 mL of fresh acetonitrile to the water sample in the 1 L flask. Again stir the contents of the flask for 15 minutes followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract. The inclusion of a few drops of salt water at this point is unimportant.

7.1.1.1.4 Add 84 mL of salt water (325 g NaCl per 1000 mL of reagent water) to the acetonitrile extract in the 100 mL volumetric flask. Add a stir bar and stir the contents on a magnetic stirrer for 15 minutes followed by 10 minutes for phase separation. Carefully transfer the acetonitrile phase to a 10 mL graduated cylinder using a Pasteur pipet. At this

stage the amount of water transferred with the acetonitrile must be minimized. The water contains a high concentration of NaCl that produces a large peak at the beginning of the chromatogram where it could interfere with the HMX determination.

7.1.1.1.5 Add an additional 1.0 mL of acetonitrile to the 100 mL volumetric flask. Again stir the contents of the flask for 15 minutes followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract in the 10 mL graduated cylinder (transfer to a 25 mL graduated cylinder if the volume exceeds 5 mL). Record the total volume of acetonitrile extract to the nearest 0.1 mL. (Use this as the volume of total extract [V_t] in the calculation of concentration after converting to µL). The resulting extract, about 5 - 6 mL, is then diluted 1:1 with reagent water prior to analysis.

7.1.1.1.6 If the diluted extract is turbid, filter it through a 0.45 - µm Teflon filter using a disposable syringe. Discard the first 0.5 mL of filtrate, and retain the remainder in a Teflon-capped vial for RP-HPLC analysis as in Section 7.4.

7.1.1.2 High-Level Method

7.1.1.2.1 Sample filtration: Place a 5 mL aliquot of each water sample in a scintillation vial, add 5 mL of acetonitrile, shake thoroughly, and filter through a 0.45-µm Teflon filter using a disposable syringe. Discard the first 3 mL of filtrate, and retain the remainder in a Teflon-capped vial for RP-HPLC analysis as in Section 7.4. HMX quantitation can be improved with the use of methanol rather than acetonitrile for dilution before filtration.

7.1.2 Soil and Sediment Samples

7.1.2.1 Sample homogenization: Dry soil samples in air at room temperature or colder to a constant weight, being careful not to expose the samples to direct sunlight. Grind and homogenize the dried sample thoroughly in an acetonitrile rinsed mortar to pass a 30 mesh sieve.

NOTE: Soil samples should be screened by Method 8510 prior to grinding in a mortar and pestle (See Safety Section 11.2).

7.1.2.2 Sample extraction

7.1.2.2.1 Place a 2.0 g subsample of each soil sample in a 15 mL glass vial. Add 10.0 mL of acetonitrile, cap with Teflon-lined cap, vortex swirl for one minute, and place in a cooled ultrasonic bath for 18 hours.

7.1.2.2.2 After sonication, allow sample to settle for 30 minutes. Remove 5.0 mL of supernatant, and combine with 5.0 mL of calcium chloride solution (Section 5.1.3) in a 20 mL vial. Shake, and let stand for 15 minutes.

7.1.2.2.3 Place supernatant in a disposable syringe and filter through a 0.45-µm Teflon filter. Discard first 3 mL and retain remainder in a Teflon-capped vial for RP-HPLC analysis as in Section 7.4.

7.2 Chromatographic Conditions (Recommended)

Primary Column:	C-18 reverse phase HPLC column, 25-cm x 4.6-mm, 5 µm, (Supelco LC-18 or equivalent).
Secondary Column:	CN reverse phase HPLC column, 25-cm x 4.6-mm, 5 µm, (Supelco LC-CN or equivalent).
Mobile Phase:	50/50 (v/v) methanol/organic-free reagent water.
Flow Rate:	1.5 mL/min
Injection volume:	100-µL
UV Detector:	254 nm

7.3 Calibration of HPLC

7.3.1 All electronic equipment is allowed to warm up for 30 minutes. During this period, at least 15 void volumes of mobile phase are passed through the column (approximately 20 min at 1.5 mL/min) and continued until the baseline is level at the UV detector's greatest sensitivity.

7.3.2 Initial Calibration. Triplicate injections of each calibration standard over the concentration range of interest are sequentially injected into the HPLC in random order. Peak heights or peak areas are obtained for each analyte. Experience indicates that a linear calibration curve with zero intercept is appropriate for each analyte. Therefore, a response factor for each analyte can be taken as the slope of the best-fit regression line.

7.3.3 Daily Calibration. Analyze midpoint calibration standards, at a minimum, in triplicate at the beginning of the day, singly at the midpoint of the run and singly after the last sample of the day (assuming a sample group of 10 samples or less). Obtain the response factor for each analyte from the mean peak heights or peak areas and compare it with the response factor obtained for the initial calibration. The mean response factor for the daily calibration must agree within ±15% of the response factor of the initial calibration. The same criteria is required

for subsequent standard responses compared to the mean response of the triplicate standards beginning the day. If this criterion is not met, a new initial calibration must be obtained.

7.4 HPLC Analysis

7.4.1 Analyze the samples using the chromatographic conditions given in Section 7.2. All positive measurements observed on the C-18 column must be confirmed by injection onto the CN column.

7.4.2 Follow Section 7.0 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence. If column temperature control is not employed, special care must be taken to ensure that temperature shifts do not cause peak misidentification.

7.4.3 Table 2 summarizes the estimated retention times on both C-18 and CN columns for a number of analytes analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

7.4.4 Record the resulting peak sizes in peak heights or area units. The use of peak heights is recommended to improve reproducibility of low level samples.

7.4.5 Calculation of concentration is covered in Section 7.0 of Method 8000.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500.

8.2 Quality control required to validate the HPLC system operation is found in Method 8000, Section 8.0.

8.3 Prior to preparation of stock solutions, acetonitrile, methanol, and water blanks should be run to determine possible interferences with analyte peaks. If the acetonitrile, methanol, or water blanks show contamination, a different batch should be used.

9.0 METHOD PERFORMANCE

9.1 Table 3 presents the single laboratory precision based on data from the analysis of blind duplicates of four spiked soil samples and four field contaminated samples analyzed by seven laboratories.

9.2 Table 4 presents the multilaboratory error based on data from the analysis of blind duplicates of four spiked soil samples and four field contaminated samples analyzed by seven laboratories.

9.3 Table 5 presents the multilaboratory variance of the high concentration method for water based on data from nine laboratories.

9.4 Table 6 presents multilaboratory recovery data from the analysis of spiked soil samples by seven laboratories.

9.5 Table 7 presents a comparison of method accuracy for soil and aqueous samples (high concentration method).

9.6 Table 8 contains precision and accuracy data for the salting-out extraction method.

10.0 REFERENCES

1. Bauer, C.F., T.F. Jenkins, S.M. Koza, P.W. Schumacher, P.H. Miyares and M.E. Walsh (1989). Development of an analytical method for the determination of explosive residues in soil. Part 3. Collaborative test results and final performance evaluation. USA Cold Regions Research and Engineering Laboratory, CRREL Report 89-9.

2. Grant, C.L., A.D. Hewitt and T.F. Jenkins (1989) Comparison of low concentration measurement capability estimates in trace analysis: Method Detection Limits and Certified Reporting Limits. USA Cold Regions Research and Engineering Laboratory, Special Report 89-20.

3. Jenkins, T.F., C.F. Bauer, D.C. Leggett and C.L. Grant (1984) Reversed-phased HPLC method for analysis of TNT, RDX, HMX and 2,4-DNT in munitions wastewater. USA Cold Regions Research and Engineering Laboratory, CRREL Report 84-29.

4. Jenkins, T.F. and M.E. Walsh (1987) Development of an analytical method for explosive residues in soil. USA Cold Regions Research and Engineering Laboratory, CRREL Report 87-7.

5. Jenkins, T.F., P.H. Miyares and ME. Walsh (1988a) An improved RP-HPLC method for determining nitroaromatics and nitramines in water. USA Cold Regions Research and Engineering Laboratory, Special Report 88-23.

6. Jenkins, T.F. and P.H. Miyares (1992) Comparison of Cartridge and Membrane Solid-Phase Extraction with Salting-out Solvent Extraction for Preconcentration of Nitroaromatic and Nitramine Explosives from Water. USA Cold Regions Research and Engineering Laboratory, Draft CRREL Special Report.

7. Jenkins, T.F., P.W. Schumacher, M.E. Walsh and C.F. Bauer (1988b) Development of an analytical method for the determination of explosive residues in soil. Part II: Further development and ruggedness testing. USA Cold Regions Research and Engineering Laboratory, CRREL Report 88-8.

8. Leggett, D.C., T.F. Jenkins and P.H. Miyares (1990) Salting-out solvent extraction for preconcentration of neutral polar organic solutes from water. Analytical Chemistry, 62: 1355-1356.

9. Miyares, P.H. and T.F. Jenkins (1990) Salting-out solvent extraction for determining low levels of nitroaromatics and nitramines in water. USA Cold Regions Research and Engineering Laboratory, Special Report 90-30.

11.0 SAFETY

11.1 Standard precautionary measures used for handling other organic compounds should be sufficient for the safe handling of the analytes targeted by Method 8330. The only extra caution that should be taken is when handling the analytical standard neat material for the explosives themselves and in rare cases where soil or waste samples are highly contaminated with the explosives. Follow the note for drying the neat materials at ambient temperatures.

11.2 It is advisable to screen soil or waste samples using Method 8510 to determine whether high concentrations of explosives are present. Soil samples as high as 2% 2,4,6-TNT have been safely ground. Samples containing higher concentrations should not be ground in the mortar and pestle. Method 8510 is for 2,4,6-TNT, however, the other nitroaromatics will also cause a color to be developed and provide a rough estimation of their concentrations. 2,4,6-TNT is the analyte most often detected in high concentrations in soil samples. Visual observation of a soil sample is also important when taken from a site expected to contain explosives. Lumps of material that have a chemical appearance should be suspect and not ground. Explosives are generally a very finely ground grayish-white material.

TABLE 1
ESTIMATED QUANTITATION LIMITS

Compounds	Water (µg/L) Low-Level	Water (µg/L) High-Level	Soil (mg/kg)
HMX	-	13.0	2.2
RDX	0.84	14.0	1.0
1,3,5-TNB	0.26	7.3	0.25
1,3-DNB	0.11	4.0	0.25
Tetryl	-	4.0	0.65
NB	-	6.4	0.26
2,4,6-TNT	0.11	6.9	0.25
4-Am-DNT	0.060	-	-
2-Am-DNT	0.035	-	-
2,6-DNT	0.31	9.4	0.26
2,4-DNT	0.020	5.7	0.25
2-NT	-	12.0	0.25
4-NT	-	8.5	0.25
3-NT	-	7.9	0.25

TABLE 2
RETENTION TIMES AND CAPACITY FACTORS ON LC-18 AND LC-CN COLUMNS

	Retention time (min)		Capacity factor (k)*	
Compound	LC-18	LC-CN	LC-18	LC-CN
HMX	2.44	8.35	0.49	2.52
RDX	3.73	6.15	1.27	1.59
1,3,5-TNB	5.11	4.05	2.12	0.71
1,3-DNB	6.16	4.18	2.76	0.76
Tetryl	6.93	7.36	3.23	2.11
NB	7.23	3.81	3.41	0.61
2,4,6-TNT	8.42	5.00	4.13	1.11
4-Am-DNT	8.88	5.10	4.41	1.15
2-Am-DNT	9.12	5.65	4.56	1.38
2,6-DNT	9.82	4.61	4.99	0.95
2,4-DNT	10.05	4.87	5.13	1.05
2-NT	12.26	4.37	6.48	0.84
4-NT	13.26	4.41	7.09	0.86
3-NT	14.23	4.45	7.68	0.88

* Capacity factors are based on an unretained peak for nitrate at 1.71 min on LC-18 and 2.00 min on LC-CN

TABLE 3
SINGLE LABORATORY PRECISION OF METHOD FOR SOIL SAMPLES

	Spiked Soils			Field-Contaminated Soils		
	Mean Conc. (mg/kg)	SD	%rsd	Mean Conc. (mg/kg)	SD	%rsd
HMX	46	1.7	3.7	14	1.8	12.8
				153	21.6	14.1
RDX	60	1.4	2.3	104	12	11.5
				877	29.6	3.4
1,3,5-TNB	8.6	0.4	4.6	2.8	0.2	7.1
	46	1.9	4.1	72	6.0	8.3
1,3-DNB	3.5	0.14	4.0	1.1	0.11	9.8
Tetryl	17	3.1	17.9	2.3	0.41	18.0
2,4,6-TNT	40	1.4	3.5	7.0	0.61	9.0
				669	55	8.2
2,4-DNT	5.0	0.17	3.4	1.0	0.44	42.3

TABLE 4
MULTILABORATORY ERROR OF METHOD FOR SOIL SAMPLES

	Spiked Soils			Field-Contaminated Soils		
	Mean Conc. (mg/kg)	SD	%rsd	Mean Conc. (mg/kg)	SD	%rsd
HMX	46	2.6	5.7	14	3.7	26.0
				153	37.3	24.0
RDX	60	2.6	4.4	104	17.4	17.0
				877	67.3	7.7
1,3,5-TNB	8.6	0.61	7.1	2.8	0.23	8.2
	46	2.97	6.5	72	8.8	12.2
1,3-DNB	3.5	0.24	6.9	1.1	0.16	14.5
Tetryl	17	5.22	30.7	2.3	0.49	21.3
2,4,6-TNT	40	1.88	4.7	7.0	1.27	18.0
				669	63.4	9.5
2,4-DNT	5.0	0.22	4.4	1.0	0.74	74.0

TABLE 5
MULTILABORATORY VARIANCE OF METHOD FOR WATER SAMPLES[a]

Compounds	Mean Conc. (µg/L)	SD	%rsd
HMX	203	14.8	7.3
RDX	274	20.8	7.6
2,4-DNT	107	7.7	7.2
2,4,6-TNT	107	11.1	10.4

[a] Nine Laboratories

TABLE 6
MULTILABORATORY RECOVERY DATA FOR SPIKED SOIL SAMPLES

	Concentration (µg/g)						
Laboratory	HMX	RDX	1,3,5-TNB	1,3-DNB	Tetryl	2,4,6-TNT	2,4-DNT
1	44.97	48.78	48.99	49.94	32.48	49.73	51.05
3	50.25	48.50	45.85	45.96	47.91	46.25	48.37
4	42.40	44.00	43.40	49.50	31.60	53.50	50.90
5	46.50	48.40	46.90	48.80	32.10	55.80	49.60
6	56.20	55.00	41.60	46.30	13.20	56.80	45.70
7	41.50	41.50	38.00	44.50	2.60	36.00	43.50
8	52.70	52.20	48.00	48.30	44.80	51.30	49.10
true conc	50.35	50.20	50.15	50.05	50.35	50.65	50.05
mean	47.79	48.34	44.68	47.67	29.24	49.91	48.32
std dev	5.46	4.57	3.91	2.09	16.24	7.11	2.78
% rsd	11.42	9.45	8.75	4.39	55.53	14.26	5.76
% diff*	5.08	3.71	10.91	4.76	41.93	1.46	3.46
mean % recovery	95	96	89	95	58	98	96

* Between true value and mean determined value.

TABLE 7
COMPARISON OF METHOD ACCURACY FOR SOIL AND AQUEOUS SAMPLES
(HIGH CONCENTRATION METHOD)

Analyte	Recovery (%) Soil Method*	Aqueous Method**
2,4-DNT	96.0	98.6
2,4,6-TNT	96.8	94.4
RDX	96.8	99.6
HMX	95.4	95.5

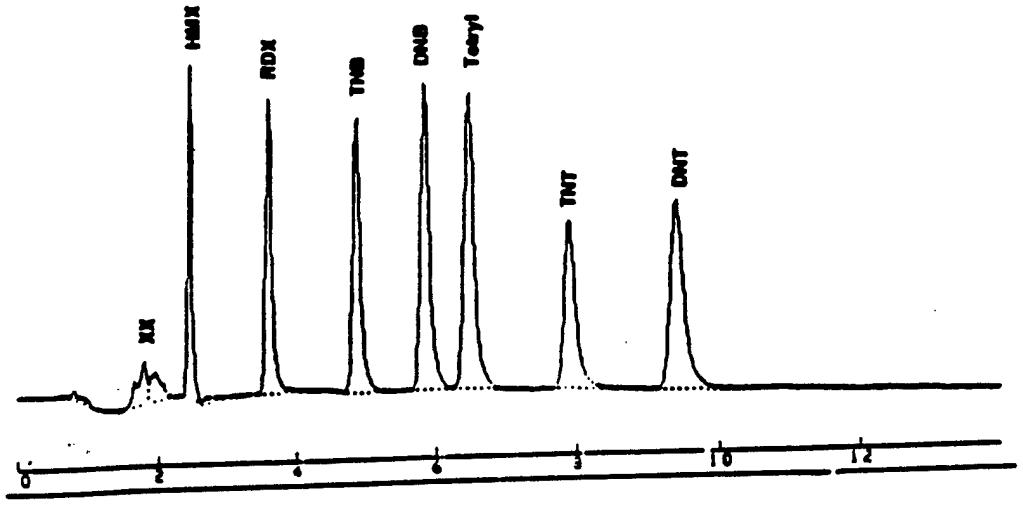
* Taken from Bauer et al. (1989), Reference 1.
** Taken from Jenkins et al. (1984), Reference 3.

TABLE 8
PRECISION AND ACCURACY DATA FOR THE SALTING-OUT EXTRACTION METHOD

Analyte	No. of Samples[1]	Precision (% RSD)	Ave. Recovery (%)	Conc. Range (µg/L)
HMX	20	10.5	106	0-1.14
RDX	20	8.7	106	0-1.04
1,3,5-TNB	20	7.6	119	0-0.82
1,3-DNB	20	6.6	102	0-1.04
Tetryl	20	16.4	93	0-0.93
2,4,6-TNT	20	7.6	105	0-0.98
2-Am-DNT	20	9.1	102	0-1.04
2,4-DNT	20	5.8	101	0-1.01
1,2-NT	20	9.1	102	0-1.07
1,4-NT	20	18.1	96	0-1.06
1,3-NT	20	12.4	97	0-1.23

[1]Reagent water

EXPLOSIVES ON A
C18 COLUMN



EXPLOSIVES ON A
CN COLUMN

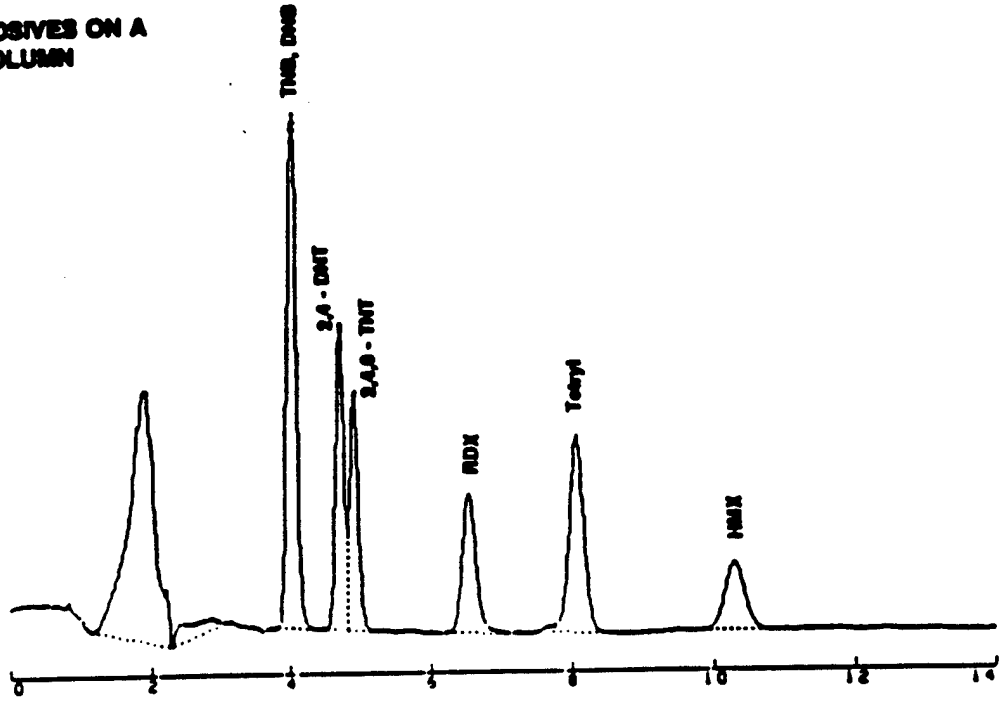
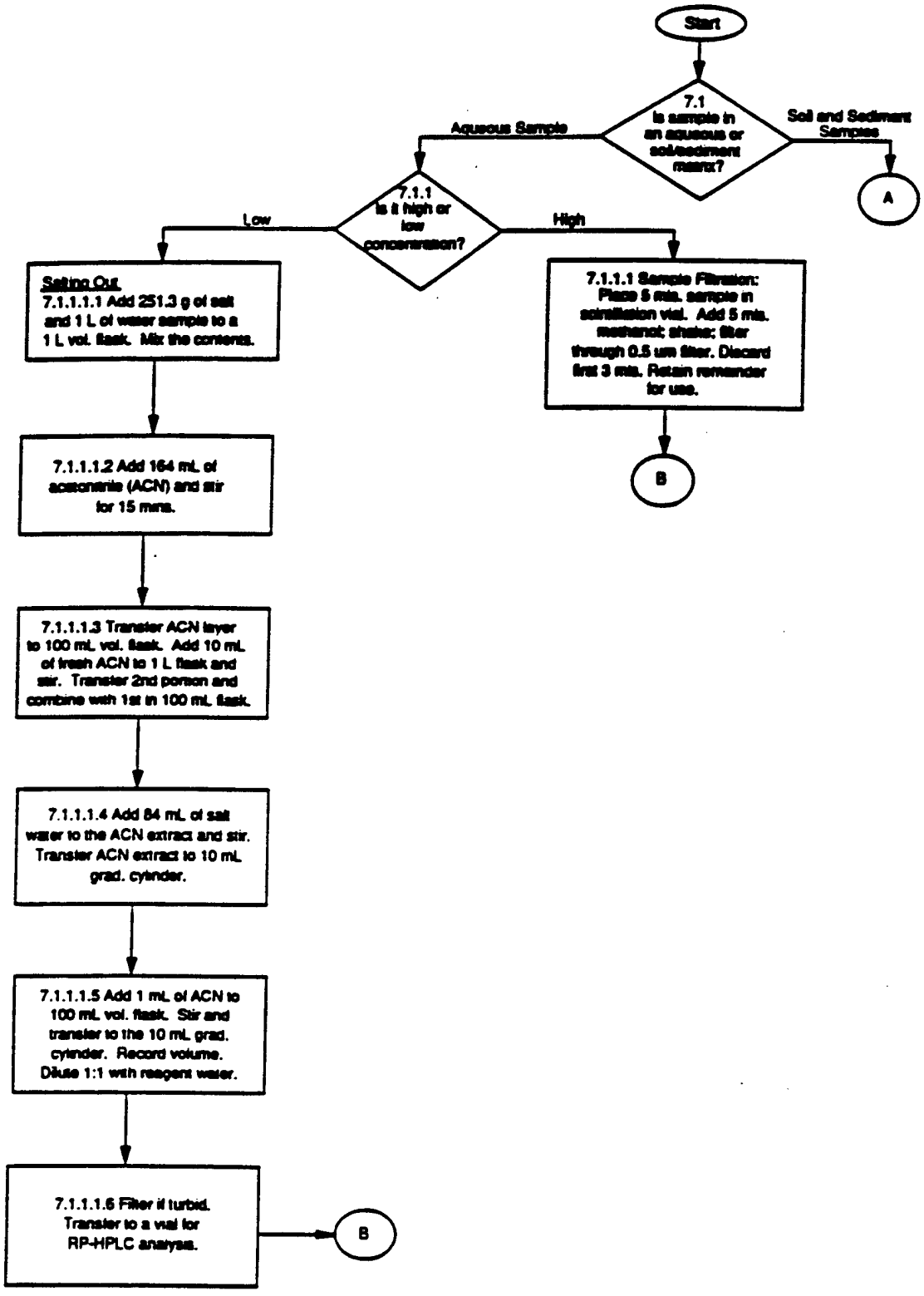
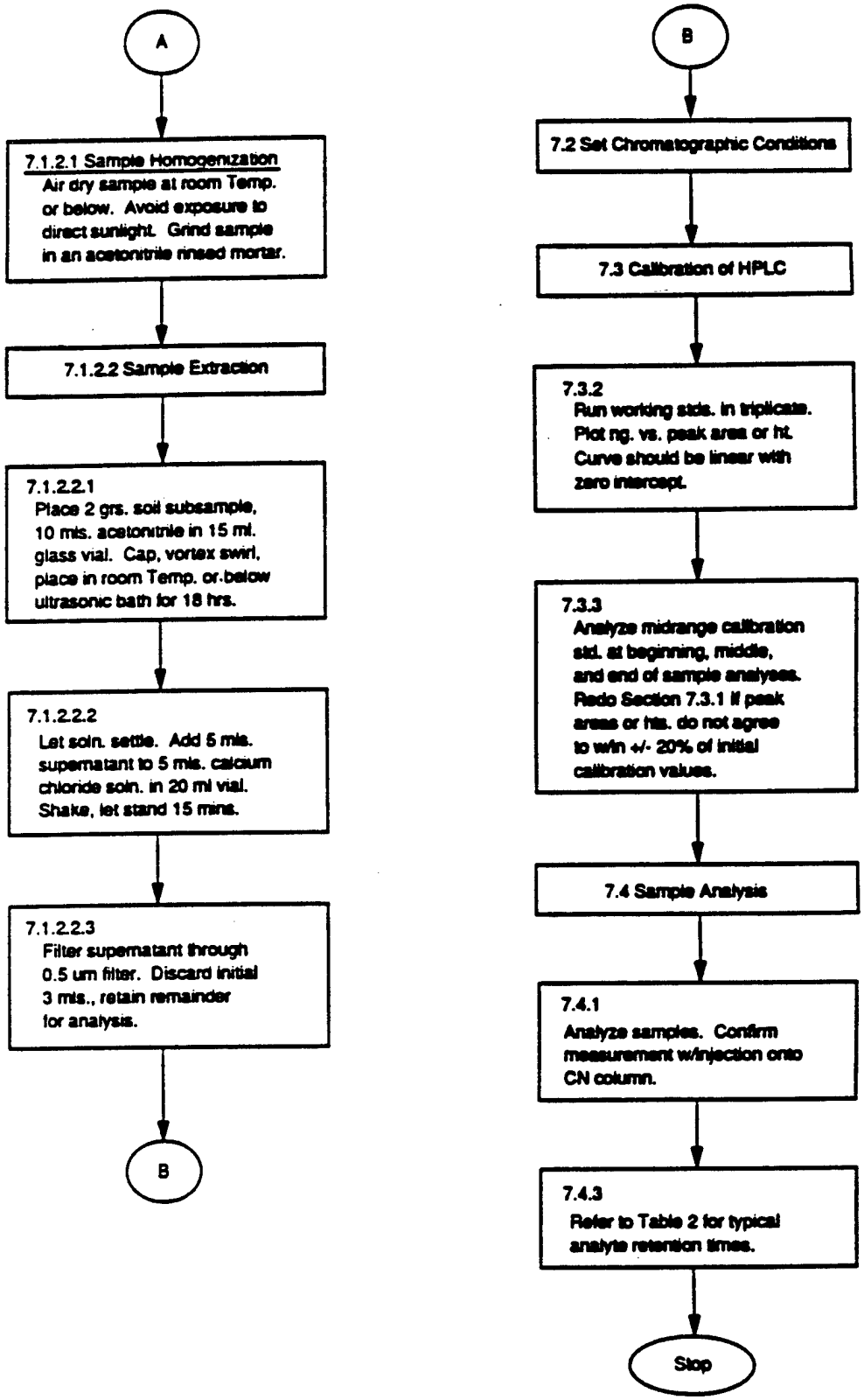


FIGURE 1
CHROMATOGRAMS FOR COLUMNS DESCRIBED IN SECTION 4.1.2.
COURTESY OF U.S. ARMY CORPS OF ENGINEERS, OMAHA, NE.


Start
7.1 Is sample in an aqueous or soil/sediment matrix?
Aqueous Sample
Soil and Sediment Samples
A
7.1.1 Is it high or low concentration?
Low
High
Salting Out
7.1.1.1.1 Add 251.3 g of salt and 1 L of water sample to a 1 L vol. flask. Mix the contents.
7.1.1.1 Sample Filtration: Place 5 mls. sample in scintillation vial. Add 5 mls. methanol; shake; filter through 0.5 um filter. Discard first 3 mls. Retain remainder for use.
7.1.1.1.2 Add 164 mL of acetonitrile (ACN) and stir for 15 mins.
B
7.1.1.1.3 Transfer ACN layer to 100 mL vol. flask. Add 10 mL of fresh ACN to 1 L flask and stir. Transfer 2nd portion and combine with 1st in 100 mL flask.
7.1.1.1.4 Add 84 mL of salt water to the ACN extract and stir. Transfer ACN extract to 10 mL grad. cylinder.
7.1.1.1.5 Add 1 mL of ACN to 100 mL vol. flask. Stir and transfer to the 10 mL grad. cylinder. Record volume. Dilute 1:1 with reagent water.
7.1.1.1.6 Filter if turbid. Transfer to a vial for RP-HPLC analysis.
B


A
7.1.2.1 Sample Homogenization
Air dry sample at room Temp. or below. Avoid exposure to direct sunlight. Grind sample in an acetonitrile rinsed mortar.
7.1.2.2 Sample Extraction
7.1.2.2.1
Place 2 grs. soil subsample, 10 mls. acetonitrile in 15 ml. glass vial. Cap, vortex swirl, place in room Temp. or below ultrasonic bath for 18 hrs.
7.1.2.2.2
Let soln. settle. Add 5 mls. supernatant to 5 mls. calcium chloride soln. in 20 ml vial. Shake, let stand 15 mins.
7.1.2.2.3
Filter supernatant through 0.5 um filter. Discard initial 3 mls., retain remainder for analysis.
B
B
7.2 Set Chromatographic Conditions
7.3 Calibration of HPLC
7.3.2
Run working stds. in triplicate. Plot ng. vs. peak area or ht. Curve should be linear with zero intercept.
7.3.3
Analyze midrange calibration std. at beginning, middle, and end of sample analyses. Redo Section 7.3.1 if peak areas or hts. do not agree to w/in +/- 20% of initial calibration values.
7.4 Sample Analysis
7.4.1
Analyze samples. Confirm measurement w/injection onto CN column.
7.4.3
Refer to Table 2 for typical analyte retention times.
Stop

APPENDIX B5

AMMONIUM PICRATE ANALYSIS

TENNESSEE VALLEY AUTHORITY

NO.: HGD-0008

TITLE: HPLC ANALYSIS OF AMMONIUM PICRATE SAMPLES

Signature	Title	Date
Prepared by: William J. Rogers	QA Officer	8-30-94
Concurred: Kathleen C. Pugh	Research Chemist	8-30-94
Concurred:		
Concurred:		
Concurred:		
Concurred:		
Approved: Joseph J. Hoagland	Team Leader Specialist Analytical Laboratory	8-30-94

REVISION				
CONTROL DATE:				

COPY NO.: _____ HAS BEEN ISSUED TO HOLDER ON _____

TVA 17207 (OPM-8-83)

Ammonium Picrate in Water and Wipe Samples by High Performance Liquid Chromatography

1.0 PURPOSE

This method is for the determination of ammonium picrate in water and wipe samples.

2.0 SCOPE

This procedure applies to work done in support of the Hot Gas Decontamination Project.

3.0 SUMMARY

Aqueous extracts from ammunition are subjected to high performance liquid chromatography (HPLC) analysis using a reverse phase column and a UV detector.

4.0 REFERENCES

"Dangerous Properties of Industrial Materials," Seventh Edition, N. Irving Sax and Richard J. Lewis, Sr., Van Nostrand Heinhold, New York

EPA RCRA Method 8000A, "Gas Chromatography"

EPA RCRA Method 8330, "Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)," Revision 0, November 1992

5.0 RESPONSIBILITIES

5.1
It is the responsibility of the supervisor to ensure this procedure is followed and that employees utilize proper safety precautions.

5.2
It is the responsibility of the technician to follow the procedure, including the safety precautions. It is the responsibility of the technician to record all data and to report unusual results to the supervisor.

6.0 REQUIREMENTS

6.1 Prerequisites

Employees handling the quantities of explosive utilized in this procedure shall have had prior safety training in the handling of explosive materials.

6.2 Apparatus

Liquid chromatograph: [a Beckman System Gold Model 126 solvent delivery system, a Beckman Model 168 photo-diode array UV detector, a

Beckman Model 501 autosampler equipped with a Rheodyne injector with a 100 uL sample loop] or [a Varian 9050 UV/Vis detector, a Varian 9012 solvent delivery system, a Varian 9100 autosampler equipped with a Valco injector and a 100 uL sample loop] or equivalent.

Liquid chromatographic column: 3.9 mm i.d. by 300 mm long stainless steel column packed with 10 um particle size reverse phase C-18 material. Alltech Versapak, or Waters u-Bondapak or equivalent. Alltech Direct Connect ® guard cartridge holder and cartridge with Versapak packing material, 4.6 mm i.d by 10 mm long, or Waters Sentry ® guard cartridge holder and cartridges with u-Bondapak packing material, or equivalent.

Filters for Mobile Phases: Millipore HA, 0.45 uM, 47 mm diameter (for Water) and Millipore FH 0.5 uM, 47 mm diameter (for Acetonitrile).

Syringe filters: Alltech 0.45 uM, 25 mm diameter PTFE, non-sterile

Sample syringes: Becton-Dickenson 3 mL or 10 mL sterile luer-lok plastic syringes

Autosampler vials: amber glass 12 x 32 mm vials with open topped caps with Teflon lined seals.

6.3 Reagents

Acetonitrile: EM Science OmniSolv, HPLC quality

Water: EM Science OmniSolv, HPLC quality

Mobile Phase Modifiers: Waters PIC A Reagent (PIC A = tetrabutylammonium phosphate, 10-15%; water, 55-60%; Methanol, 25-30%; potassium phosphate, monobasic, 1-5%; and potassium hydroxide, 1-5%) or equivalent.

Tetrabutylammonium dihydrogen phosphate (TBADP), 97% (Fluka or Aldrich).

Mobile phase solutions: Solution A: Add one bottle of PIC A reagent (15 mL) to 1000 mL of OmniSolv water. Stir for 5 minutes and then filter through a 0.45-micron filter type HA for aqueous solvents.

Solution B: Allow 1.698 g (0.005 M) Tetrabutylammonium dihydrogen phosphate

to dissolve in about 400 mL acetonitrile then dilute to a final volume of 1,000 mL with acetonitrile. Stir for 5 minutes and then filter through 0.5-micron filter type FH for organic solvents.

Picric acid calibration standards: analytical reference grade or highest purity available. These shall be obtained from military sources.

Picric Acid for QA/QC: analytical reference grade or highest purity available. These may be obtained from chemical specialty suppliers.

6.4 Analysis by HPLC

CAUTION: Wear suitable gloves (that is, gloves impenetrable to the solvents being used, such as 35 mil butyl gloves for acetonitrile) while performing the following steps. Avoid inhaling fumes. Work in an area with adequate ventilation.

CAUTION: Wear eye protection to prevent splashes from getting in the eye.

CAUTION: Some of the solvents are flammable and very volatile. Do not use near heat, sparks, or ignition. Keep containers tightly closed when not in use.

CAUTION: In case of skin exposure, wash immediately with soap and water.

6.4.1 The following chromatographic conditions have been found to be suitable for this analysis:

Mobile phase: The separation is made under isocratic conditions. Using the solvent programmer, combine 36 % solution A with 64% solution B.

Isocratic: 36% [Water + PIC A] + 64% [Acetonitrile + TBADP]

Flow rate: 1.10 mL/min

Detection: 254 nm (365 nm is also possible)

Sample Loop: 100 uL

6.4.2 Sample Preparation: Samples (including calibration standards and calibration checks) shall be diluted 1:1 with mobile phase solution B (acetonitrile and tetrabutylammonium dihydrogen phosphate). That is, 1.0 mL of sample shall be mixed with 1.0 mL solution B. Samples shall be

allowed to warm to room temperature for 10 minutes.Samples shall be filtered through syringe filters prior to analysis and placed in 1.5 mL HPLC autosampler vials.

6.4.3 Calibration: shall be done in accordance with EPA RCRA Method 8000A, modified as follows:

6.4.4 External standard calibration procedure: Picric acid calibration standards shall be prepared at a minimum of five concentrations by weighing a stock standard and diluting with an appropriate weight of water. One standard shall be at a concentration approximately equal to the method detection limit. The other concentrations shall correspond to the expected range of concentrations found in real samples (anticipated to be 0.01-1.0 ppm) or should define the working range of the detector.

Each calibration standard shall be injected using the standard techniques used to introduce actual samples to the HPLC (e.g. autosampler injections using the 100 uL sample loop). The calibration shall be performed in triplicate in random order. The calibration shall not be forced through the origin. The ratio of the response (peak height) to the amount of analyte injected, defined as the response factor, shall be calculated for picrate. The results shall be used to prepare a calibration curve for picrate.

At the beginning of each day, the midpoint calibration standard will be analyzed in triplicate. The response factor for the average of these three points must be within ± 15 % of the response factor for the initial calibration. If not, the machine will be recalibrated. Then at least every ten samples and at the end of the run, a single midpoint calibration standard will be run. The response factors for these must be within ± 15 % of the mean daily initial response factor. If a midpoint calibration check falls outside the 15 % limits, all samples after the last valid calibration check will be reanalyzed.

6.4.5 Alternate Calibration for Unstable Operating Conditions Calibration will be performed with standards of five concentrations at the beginning of each day, run singly. A midpoint calibration standard will be run at least every 10 samples and at the end of the run throughout the day. Any group of ten samples following a midpoint calibration check which falls outside the 15 percent limits will be reanalyzed, as well as the group of ten samples prior to the failed calibration check sample.

6.4.6 Retention Time Windows: Before establishing windows, the HPLC system shall be fully equilibrated to working conditions. Three injections of a picrate standard shall be made.

The retention time window will be set at ± 5 % of the average, absolute retention time may also be used to define the retention time window. (For example, a retention time of 4.00 minutes would have a window of 3.80-4.20 minutes.) The method generating the larger window shall be used. When a new column is installed, retention time windows must be redetermined.

If the retention time of picrate during daily calibration verification falls outside the established window, a new retention time shall be determined, which will necessitate a recalibration.

6.4.7 Method Detection Limits: will be determined in accordance with 40 CFR 136 Appendix B, Revision 1.11 with the equation for variance corrected.

6.4.8 Column Washing and Storage: after sample runs are complete and no further samples are anticipated for 72 hours, the column shall be washed with solvents with no modifiers for 2 hours with 90% water / 10% organic solvent (depending on column packing, either acetonitrile or methanol) at 1.0 mL/min. The column shall then be washed for 1 hour with 90% organic solvent/10% water at 1.0 mL/min. The column shall then be washed for 2 hours with the manufacturer recommended storage solution at 1.0 mL/min. (Versapak requires 42% water/58% acetonitrile, u-Bondapak requires 100% methanol). At the analyst's discretion, more thorough manufacturer recommended column washing protocols may be used.

7.0 QUALITY ASSURANCE PROVISIONS

7.1 Responsibility of Inspection

It shall be the responsibility of the technician to inspect HPLC mobile phases for precipitation prior to use. All visible precipitation shall be removed prior to use by filtration.

7.2 Acceptance Criteria

Calibration curves shall have coefficients of determination of 0.999 or greater.

After every ten (10) samples, a mid-point calibration check sample shall be run. If the calibration check sample is not reported as within ± 15% of the expected value, and basic trouble-shooting does not improve the results, a recalibration shall be performed and the previous ten runs shall be reanalyzed.

7.3 Material Monitoring

None

7.4 Equipment Monitoring

The technician shall inspect the HPLC chromatograph for any problems such as leaks, pressure irregularities, or other malfunctions on an ongoing basis.

7.5 Certification

A quality control check sample,at approximately the mid-point of the calibration curve, which will have been produced independently from the calibration standards and which contains picrate (in the form of picric acid), will be analyzed four times. The average recovery and the standard deviation will be calculated. The mean must fall within 4% of the known value and the relative standard deviation of the data set should be < 4%

7.6 Quality Control Sample Requirements

7.6.1 Method Accuracy and Precision A quality control check sample, which will have been produced independently from the calibration standards and which contains picrate (in the form of picric acid), will be analyzed eight (8) times initially. The average recovery and the standard deviation will be calculated. Single quality control check samples will be run with each sample run thereafter and a control chart with analysis values shall be established for picrate analysis using this method.

7.6.2 Batch QC

7.6.3 Definitions

Batch - A group of no more than 20 samples of the same matrix prepared or extracted at the same time with the same reagents.

Note: If ALSS determines that extracts of smears (wipe samples) are similar in behavior to extract samples, they may be counted as the same matrix for determining batch break points.

Method Blank - A sample of clean reagent carried through preparation and extraction in the same manner as samples.

Matrix Spike - An aliquot of a sample spiked with a known concentration of all target analytes. Spike concentration is set to read at five times the method quantitation limit in the sample. One matrix spike is run for each batch. Spiking occurs prior to sample preparation and analysis except for spike samples made for smear samples. Smear spikes will be made by extracting

the actual sample, withdrawing an aliquot of the extract solution, adding the spike to that aliquot, then diluting to volume.

Matrix Spike Duplicate - A second aliquot of the same sample treated as the matrix spike.

Quality Control Check Sample - A sample containing mid-range concentrations of analytes of interest with concentrations known to the analyst. This sample is made from a separate stock of standard material than calibration and spiking solutions when possible.

Duplicate - A second aliquot of a sample.

7.6.4 Batch QC Samples

One matrix spike will be run with each batch.

One duplicate or matrix spike duplicate will be run with each batch.

One method blank will be run with each batch.

One quality control check sample will be run with each batch.

Whenever the sampling organization in the field submits additional samples as quality control checks (as is defined in the sampling plan of the test program, contained in the body of this report), ALSS will count these as samples in determining batch size.

8.0 SAFETY

8.1 Solvents utilized in this procedure have some hazards associated with them as summarized below. Also refer to any Material Safety Data Sheets present in the work area.

8.1.2 Acetonitrile is a flammable liquid which is poisonous by ingestion and intraperitoneal routes. It is a skin and severe eye irritant. It is a dangerous fire hazard when exposed to heat, flame, or oxidizers. OSHA Permissible Exposure Limit is 40 ppm (70 mg/m3). The Short Term Exposure Limit is 60 ppm.

8.1.3 This solvent should be used in the hood whenever possible. If an odor is detected, wear a respirator.

8.1.4 In case of skin contact, wash immediately with soap and water.

8.1.5 In case of eye contact, flush immediately with water, holding the eyes open to ensure they are rinsed.

8.1.6 Gloves impenetrable to the particular solvent must be worn when handling it.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICES

APPENDIX B6

DUCT GAS SAMPLING

HOT GAS DECONTAMINATION CHAMBER DISCHARGE DUCT GAS SAMPLING REPORT OUTLINE

1.0 Introduction

A sampling train based on the EPA's Modified Method 5 sampling train was used to collect samples of the off-gas leaving the Hot Gas Decontamination Chamber.

2.0 Sampling Train

2.1 Sampling train schematic: Schematics of the sampling trains used are shown in figures 1 and 2.

2.2 Probe: Stainless Steel 3/8" ID, with a 90° elbow on one end and a stainless steel 28/15 socket joint on the other end.

2.3 Resin Tube: Glass, 5/8" ID x 9 1/2" long.

2.4 Impingers: Four 500-mL impingers, connected in series with leak-free ground-glass joints. The first, third, and forth impingers were of the Greenburg-Smith design modified by replacing the tip with a 1/2-in. ID glass tube extending about 1/2-in. from the bottom of the outer cylinder. The second impinger was of the Greenburg-Smith design with the standard tip.

2.5 Vacuum pump: Leak-free, capable of maintaining a sampling rate of approximately one cubit foot per minute.

2.6 Dry gas meter: *Sprague*, Textron Model 175

2.7 Flow meter: *Dwyer*, RMB Series, catalog number RMB-53-SS, 10-100 SCFH AIR.

2.8 Stack gas velocity determination equipment:

2.8.1 Manometer: *Dwyer*, Model 400-10, 0-10 inches of water.

2.8.2 Pitot Tube: *Dwyer*, Model 160S-36, "S" Type, Stainless Steel, 36" long.

2.8.3 Temperature Sensor: *Omega*, Model HH21, Digital Thermometer, with a "K" type, grounded junction, model CAIN-14G-18 thermocouple assembly .

3.0 Sampling Reagents

3.1 Impinger reagents: The first three impingers were empty, while the fourth impinger contained indicating type, 6-16 mesh silica gel.

3.2 Resin tube: TENAX TA, 20/35 mesh.
(See attachment 1, test 2, 3, and 4)

4.0 Sampling Procedure

4.1 Sample train preparation: All glassware in front of the resin tube was washed and rinsed with acetonitrile before each use. Silica gel was placed in one of the modified Greenburg-Smith design impingers. The other three were used empty. All four impingers were weighed to obtain a tare weight. After the test, the impingers were reweighed to determine the stack-gas moisture content. The impingers were connected in series with leak-free ground-glass joints with the first, third, and fourth being of the Greenburg-Smith design with the modified tip and the second being of the Greenburg-Smith design with the standard tip. A light coat of stopcock grease was used on all ground-glass joints. The impinger with the silica gel was placed in the fourth position. Three to four grams of resin was weighed and placed into the glass tube for each test. During the first few tests, the resin tube was placed between the probe and the first impinger (see figure 1). The resin tube was then moved between the third and fourth impingers to allow the gas to cool before entering into the resin tube (see figure 2). Ice was maintained around the inpingers during the tests.

4.2 Leak check: Before each test was begun, a leak check was performed on the assembled collection train.

4.3 Sample train operation: The sample probe was attached to the duct so that the tip was located in the center of the duct with the tip opening facing into the gas stream. The sample train was assembled as shown in either figure 1 or figure 2. After all connections were made, the vacuum pump was started and the flow rate was adjusted to obtain the desired sampling rate using the flowmeter as a guide. A constant sampling rate was maintained during the entire sample run. The required data was recorded on the field data sheet.

4.4 Velocity traverse: Velocity traverses were taken during each test. A total of twelve points were used to traverse the stack cross section.

4.5 Sample recovery: After disassembling the sample train, the resin tube was capped for shipment to the analytical laboratory. The impingers were weighed for moisture determination. All of the glassware before the silica gel impinger was rinsed with acetonitrile. The acetonitrile wash was placed in a bottle and shipped to the analytical laboratory.

5.0 Calibration

Metering system: *American Meter*, wet test meter, stainless, size AL-19, one cubit foot per revolution, serial number 17299, was used to calibrate the dry gas meter.

6.0 Calculations

$$v_s = K_p C_p (dp)^{1/2}_{avg} (T_{s(avg)}/P_s M_s)^{1/2}$$

$$Q_{sd} = 3600(1-B_{ws}) v_s A (T_{std}/T_{s(avg)})(P_s/P_{std})$$

Where: v_s = Average stack gas velocity.
K_p = Pitot tube constant = 85.49 ft/sec[(lb/lb-mole)(in. Hg)/(°R)(in. H_2O)]$^{1/2}$.
C_p = Pitot tube coefficient, dimensionless = 0.84.
dp = Velocity head of stack gas, in. H_2O.
T_s = Absolute stack temperature, °R.
P_s = Absolute stack gas pressure, in. Hg.
M_s = Molecular weight of stack gas, wet basis, lb/lb-mole.
Q_{sd} = Average stack gas dry volumetric flow rate.
B_{ws} = Water vapor in gas stream, proportion by volume.
A = Cross sectional area of stack, ft^2.
T_{std} = Standard absolute temperature, 528°K.
P_{std} = Standard absolute pressure, 29.92 in. Hg.

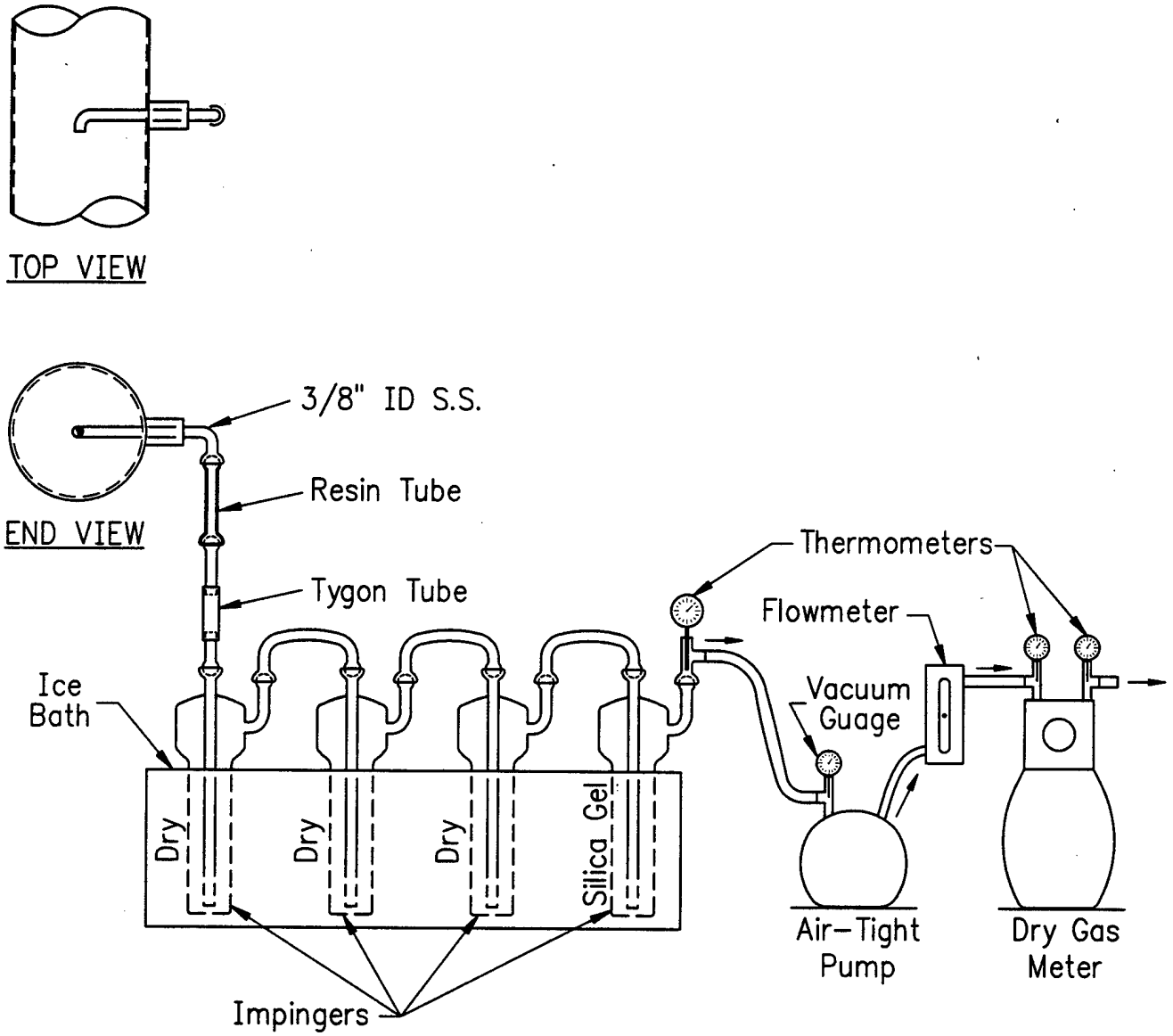

TOP VIEW
END VIEW
3/8" ID S.S.
Resin Tube
Tygon Tube
Ice Bath
Dry
Dry
Dry
Silica Gel
Impingers
Thermometers
Flowmeter
Vacuum Guage
Air-Tight Pump
Dry Gas Meter

Figure 1

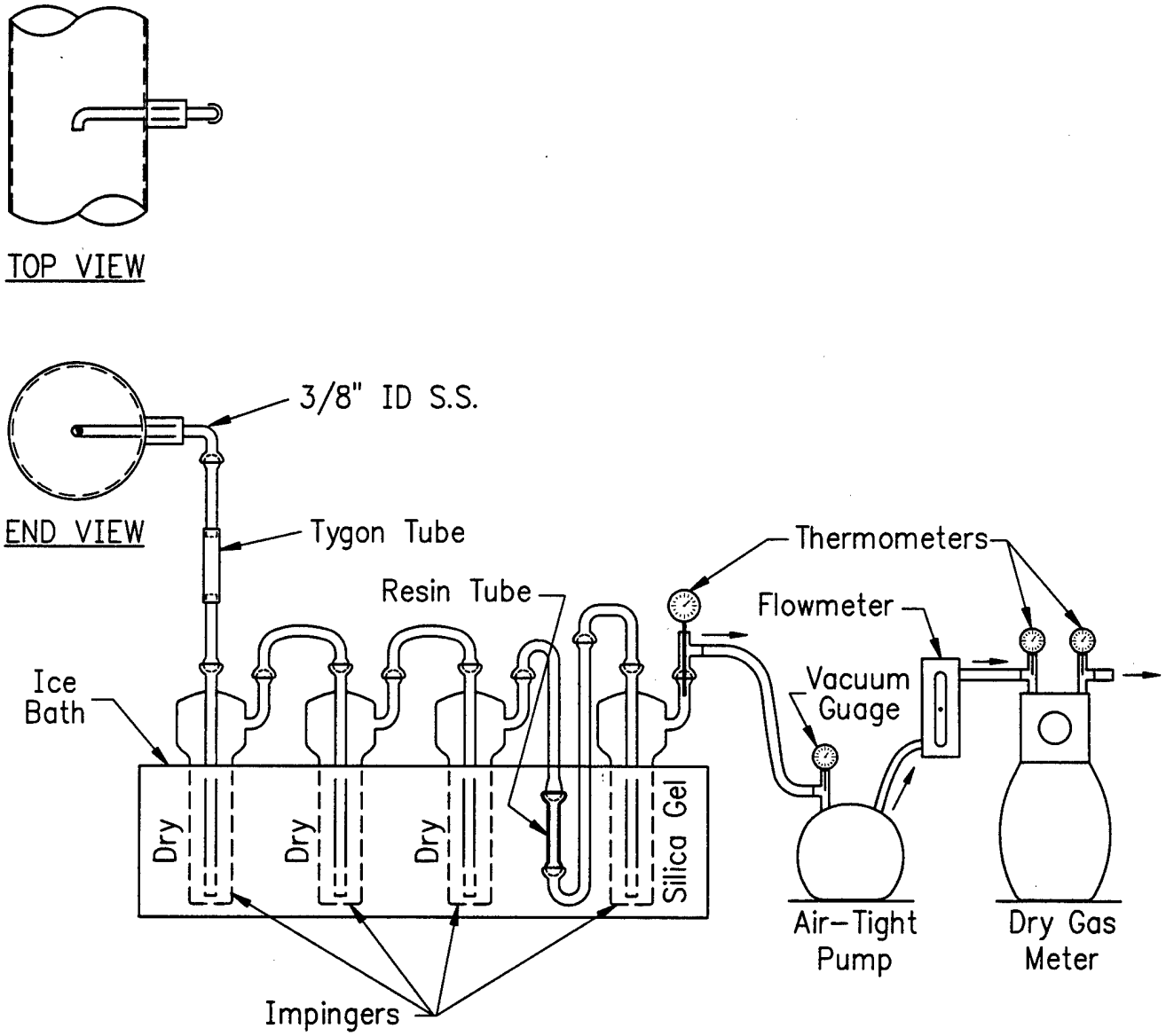

TOP VIEW
END VIEW
3/8" ID S.S.
Tygon Tube
Resin Tube
Thermometers
Flowmeter
Vacuum
Guage
Ice
Bath
Dry
Dry
Dry
Silica Gel
Air-Tight
Pump
Dry Gas
Meter
Impingers

Figure 2

FIELD DATA

Plant _____
Location _____
Operators _____
Date _____
Run No. _____
Pump No. _____
Dry Gas Meter No. _____
Flow Meter No. _____
Pitot Tube Coefficient, Cp = 0.84

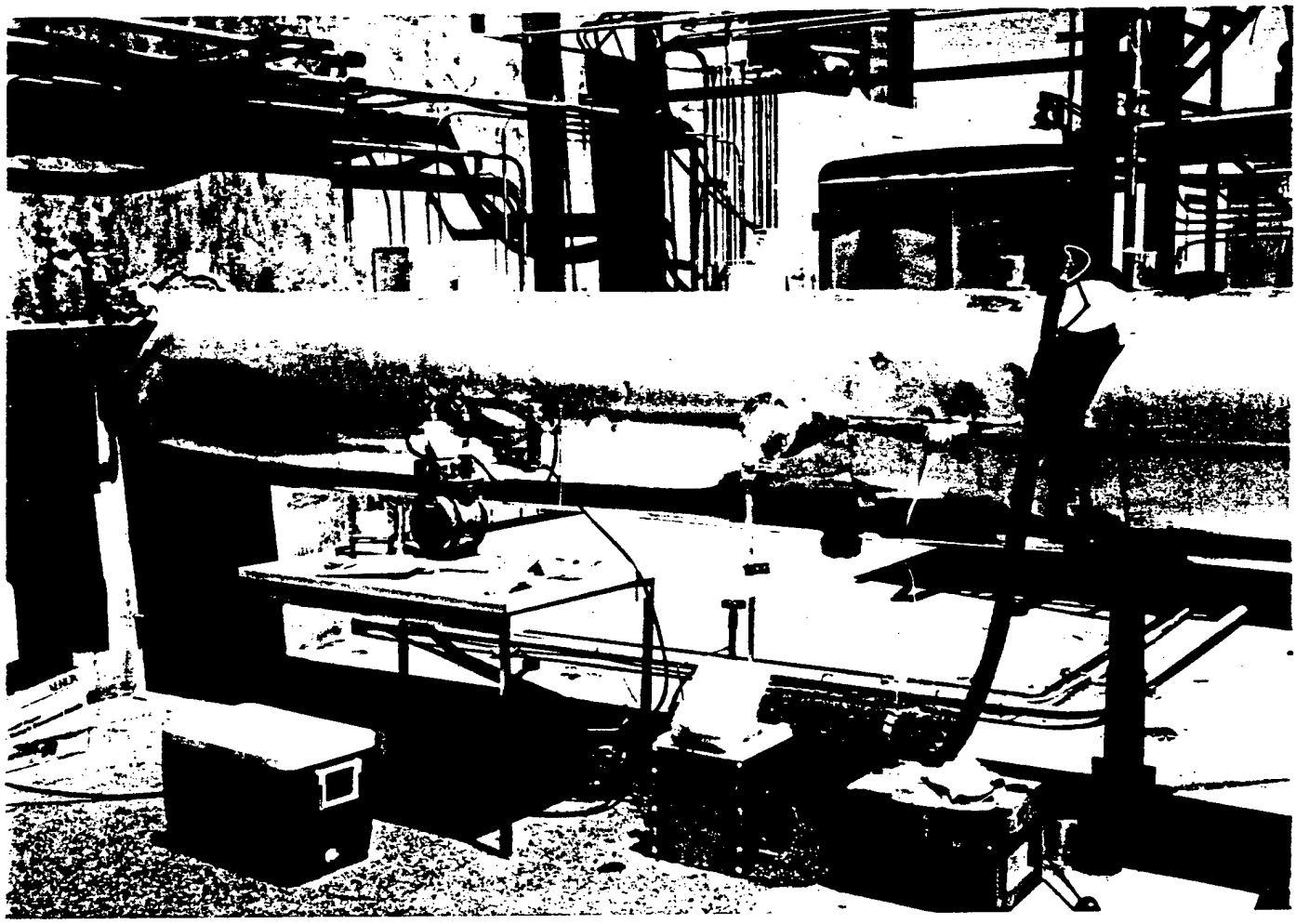
Schematic of Stack Cross Section

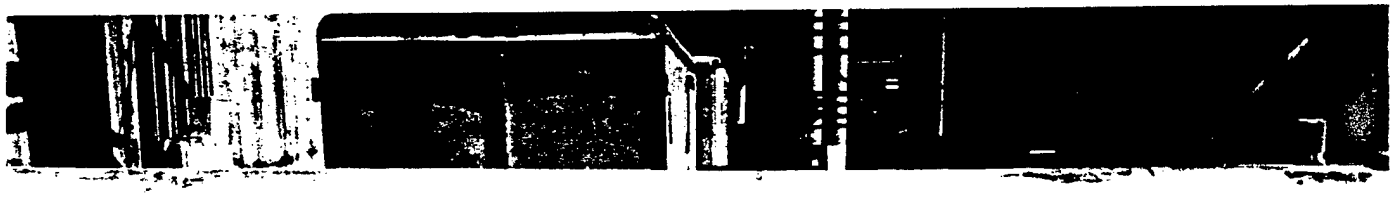
Ambient Temperature _____
Barometric Pressure _____
Static Pressure, in Hg _____

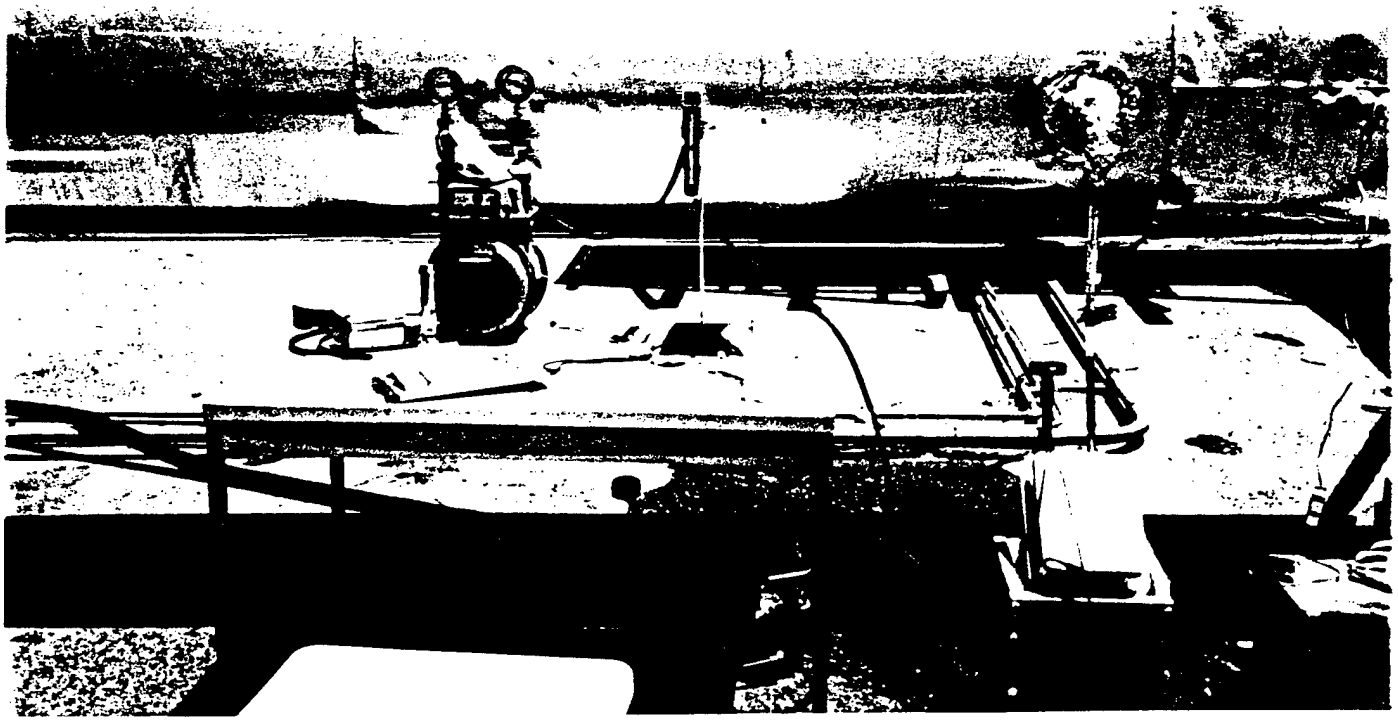
Sample Tube No. _____
Sample Box No. _____
Impinger Nos. _____

Traverse Point Number	Sampling Time (O) min.	Vacuum in. Hg	Stack Temp. (Ts) °F	Velocity Head (•Ps) in. H2O	Flowmeter SCFM	Gas Sample Volume Cu. ft.	Gas Sample Temperatuer At Dry Gas Meter			Temp. of Gas Leaving Last Impinger °F
							Inlet °F	Outlet °F		
H - 1										
H - 2										
H - 3										
H - 4										
H - 5										
H - 6										
V - 1										
V - 2										
V - 3										
V - 4										
V - 5										
V - 6										
Total										
Average										

Figure 3







PREPARATION OF XAD-2 SORBENT RESIN

1.0 SCOPE AND APPLICATION

1.1 XAD-2 resin as supplied by the manufacturer is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Both the salt solution and any residual extractable monomer and polymer species must be removed before use. The resin is prepared by a series of water and organic extractions, followed by careful drying.

2.0 EXTRACTION

2.1 Method 1: The procedure may be carried out in a giant Soxhlet extractor. An all-glass thimble containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenellated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass-wool plug and stainless steel screen because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with Type II water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with H_2O for 8 hr.
Methyl alcohol	Extract for 22 hr.
Methylene chloride	Extract for 22 hr.
Methylene chloride (fresh)	Extract for 22 hr.

2.2 Method 2:

2.2.1 As an alternative to Soxhlet extraction, a continuous extractor has been fabricated for the extraction sequence. This extractor has been found to be acceptable. The particular canister used for the apparatus shown in Figure A-1 contains about 500 g of finished XAD-2. Any size may be constructed; the choice is dependent on the needs of the sampling programs. The XAD-2 is held under light spring tension between a pair of coarse and fine screens. Spacers under the bottom screen allow for even distribution of clean solvent. The three-necked flask should be of sufficient size (3-liter in this case) to hold solvent

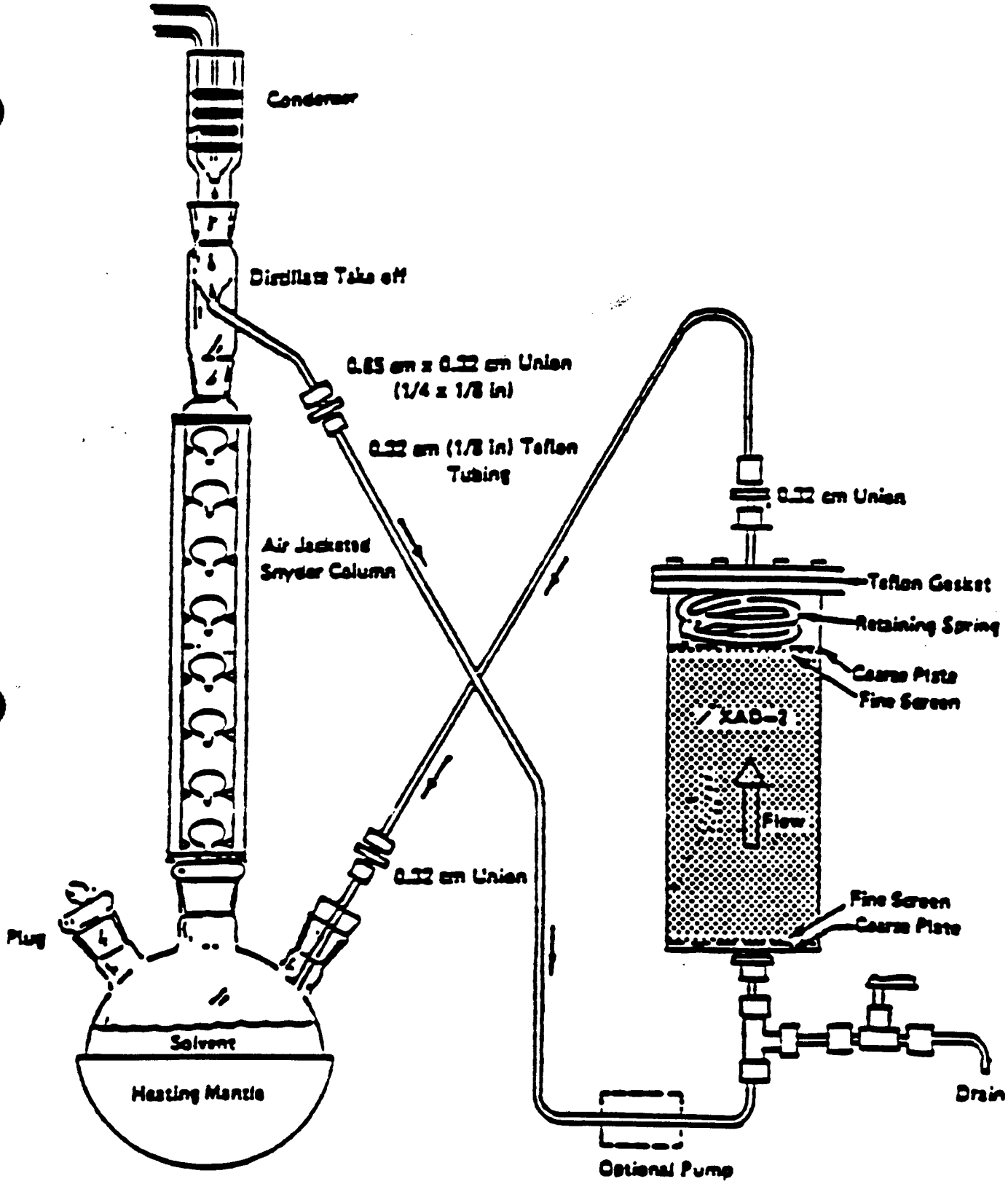


Figure A-1. XAD-2 cleanup extraction apparatus.

equal to twice the dead volume of the XAD-2 canister. Solvent is refluxed through the Snyder column, and the distillate is continuously cycled up through the XAD-2 for extraction and returned to the flask. The flow is maintained upward through the XAD-2 to allow maximum solvent contact and prevent channeling. A valve at the bottom of the canister allows removal of solvent from the canister between changes.

2.2.2 Experience has shown that it is very difficult to cycle sufficient water in this mode. Therefore the aqueous rinse is accomplished by simply flushing the canister with about 20 liters of distilled water. A small pump may be useful for pumping the water through the canister. The water extraction should be carried out at the rate of about 20-40 mL/min.

2.2.3 After draining the water, subsequent methyl alcohol and methylene chloride extractions are carried out using the refluxing apparatus. An overnight or 10- to 20-hr period is normally sufficient for each extraction.

2.2.4 All materials of construction are glass, Teflon, or stainless steel. Pumps, if used, should not contain extractable materials. Pumps are not used with methanol and methylene chloride.

3.0 DRYING

3.1 After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proved to be the fastest and most reliable drying method.

3.2 A simple column with suitable retainers, as shown in Figure A-2, will serve as a satisfactory column. A 10.2-cm (4-in.) Pyrex pipe 0.6 m (2 ft) long will hold all of the XAD-2 from the extractor shown in Figure A-1 or the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum resin load at the exit of the column.

3.3 Method 1: The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has routinely proved to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95-cm (3/8-in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2 may be dried overnight by consuming a full 160-liter cylinder of liquid nitrogen.

3.4 Method 2: As a second choice, high-purity tank nitrogen may be used to dry the XAD-2. The high-purity nitrogen must first be passed through a bed

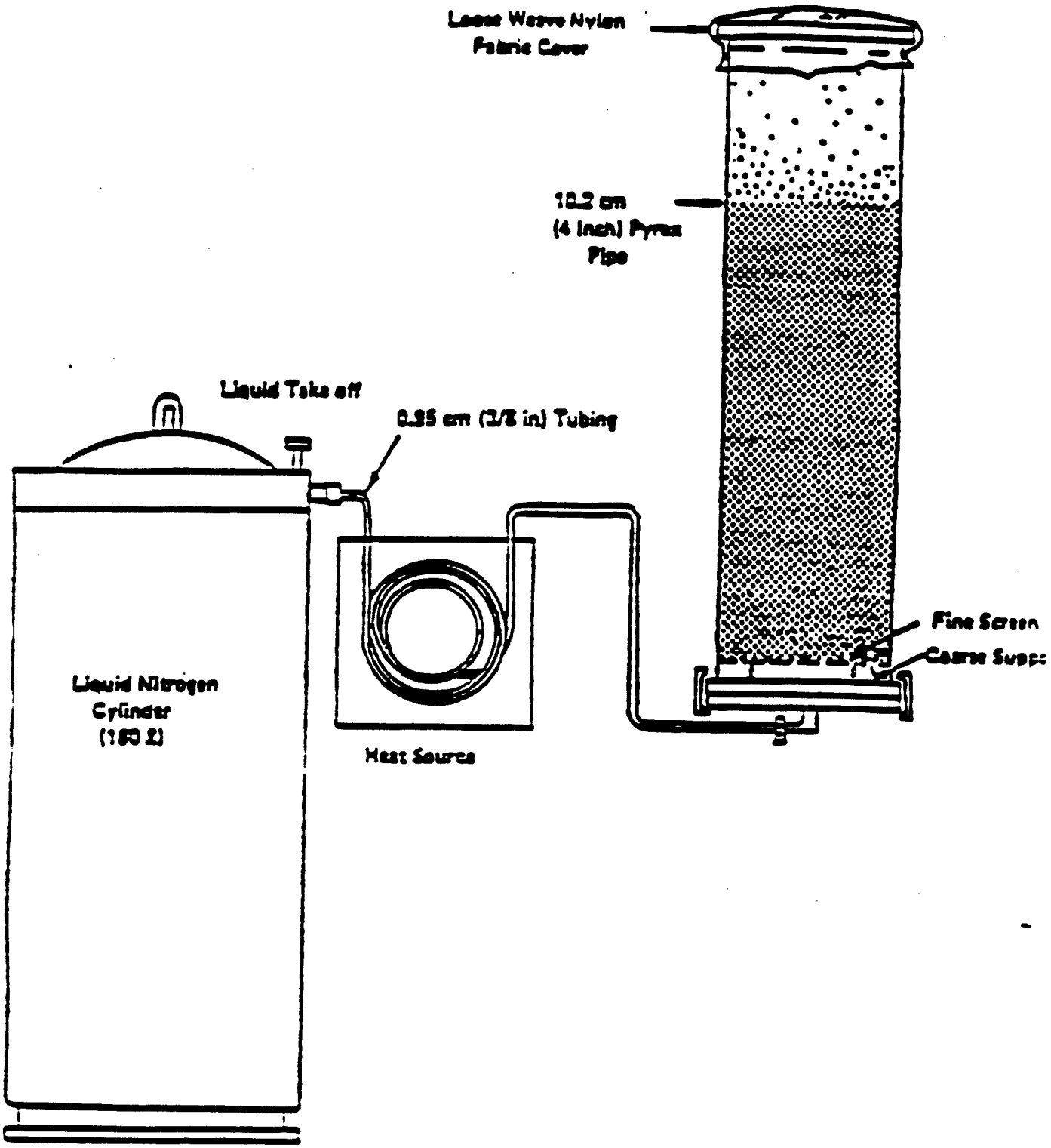


Figure A-2. XAD-2 fluidized-bed drying apparatus.

Revision 0
Date September 1986

of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidization may cause the particles to break up.

4.0 QUALITY CONTROL PROCEDURES

4.1 For both Methods 1 and 2, the quality control results must be reported for the batch. The batch must be reextracted if the residual extractable organics are >20 ug/mL by TCO analysis or the gravimetric residue is >0.5 mg/20 g XAD-2 extracted. (See also section 5.1, Method 0010.)

4.2 Four control procedures are used with the final XAD-2 to check for (1) residual methylene chloride, (2) extractable organics (TCO), (3) specific compounds of interest as determined by GC/MS, as described in Section 4.5 below, and (4) residue (GRAV).

4.3 Procedure for residual methylene chloride:

4.3.1 **Description:** A 1±0.1-g sample of dried resin is weighed into a small vial, 3 mL of toluene are added, and the vial is capped and well shaken. Five uL of toluene (now containing extracted methylene chloride) are injected into a gas chromatograph, and the resulting integrated area is compared with a reference standard. The reference solution consists of 2.5 uL of methylene chloride in 100 mL of toluene, simulating 100 ug of residual methylene chloride on the resin. The acceptable maximum content is 1,000 ug/g resin.

4.3.2 **Experimental:** The gas chromatograph conditions are as follows:

6-ft x 1/8-in. stainless steel column containing 10% OV-101 on 100/120 Supelcoport;

Helium carrier at 30 mL/min;

FID operated on 4 x 10^{-11} A/mV;

Injection port temperature: 250°C;

Detector temperature: 305°C;

Program: 30°C(4 min) 40°C/min 250°C (hold); and

Program terminated at 1,000 sec.

4.4 Procedure for residual extractable organics:

4.4.1 **Description:** A 20±0.1-g sample of cleaned, dried resin is weighed into a precleaned alundum or cellulose thimble which is plugged with cleaned glass wool. (Note that 20 g of resin will fill a thimble, and the

resin will float out unless well plugged.) The thimble containing the resin is extracted for 24 hr with 200-mL of pesticide- grade methylene chloride (Burdick and Jackson pesticide-grade or equivalent purity). The 200-mL extract is reduced in volume to 10-mL using a Kuderna-Danish concentrator and/or a nitrogen evaporation stream. Five uL of that solution are analyzed by gas chromatography using the TCO analysis procedure. The concentrated solution should not contain >20 ug/mL of TCO extracted from the XAD-2. This is equivalent to 10 ug/g of TCO in the XAD-2 and would correspond to 1.3 mg of TCO in the extract of the 130-g XAD-2 module. Care should be taken to correct the TCO data for a solvent blank prepared (200 mL reduced to 10 mL) in a similar manner.

4.4.2 Experimental: Use the TCO analysis conditions described in the revised Level 1 manual (EPA 600/7-78-201).

4.5 GC/MS Screen: The extract, as prepared in paragraph 4.4.1, is subjected to GC/MS analysis for each of the individual compounds of interest. The GC/MS procedure is described in Chapter Four, Method 8270. The extract is screened at the MDL of each compound. The presence of any compound at a concentration >25 ug/mL in the concentrated extract will require the XAD-2 to be recleaned by repeating the methylene chloride step.

4.6 Methodology for residual gravimetric determination: After the TCO value and GC/MS data are obtained for the resin batch by the above procedures, dry the remainder of the extract in a tared vessel. There must be <0.5 mg residue registered or the batch of resin will have to be extracted with fresh methylene chloride again until it meets this criterion. This level corresponds to 25 ug/g in the XAD-2, or about 3.25 mg in a resin charge of 130 g.

APPENDIX B7

WIPE SAMPLING TECHNIQUE

TENNESSEE VALLEY AUTHORITY

NO.: HGD-0007

TITLE: ~~TVA~~ WIPE SAMPLING TECHNIQUE

Signature	Title	Date
Prepared by: William J. Rogers	QA Officer	5/25/94
Concurred: Kathleen C. Pugh	Research Chemist	7/19/94
Concurred:		
Concurred:		
Concurred:		
Concurred:		
Approved: Joe J. Hoagland	Team Leader Specialist Analytical Laboratory	7/14/94

REVISION	R0			
CONTROL DATE:				

COPY NO.: _____ HAS BEEN ISSUED TO HOLDER ON _____

TVA 17207 (OPM-8-83)

SECTION 13

SPECIALIZED SAMPLING TECHNIQUES

13.0 GENERAL

This section discusses several specialized sampling techniques that have been used by contractors on hazardous waste sites. The reader may develop other techniques for specific site needs. In those cases and in cases where the techniques listed here are modified for use on a specific site, careful documentation of the exact procedures used should be provided. This section does not discuss analytical techniques, since analytical methods would vary depending on the data quality objectives, the compounds of concern, the media, and the exact sampling technique. The Contract Laboratory Program plans to issue a "Field Methodology Catalog" in the summer of 1987 that will contain field analytical techniques suitable for analyses of the samples collected by using the techniques in this section.

13.1 WIPE SAMPLING

13.1.1 Scope and Purpose

This guideline discusses the steps required for obtaining a wipe sample. Wipe samples may be used to document the presence of carcinogenic substances or other toxic materials. In addition, wipe sampling is commonly used to ascertain that site or equipment decontamination has been acceptably effective.

13.1.2 Definitions

Site Manager (SM)

The individual responsible for the successful completion of a work assignment within budget and schedule. This person is also referred to as the Site Project Manager or the Project Manager and is typically a contractor's employee (see Subsection 1.1).

Wipe Sample

A sample used to assess surface contamination. The terms "wipe sample," "swipe sample," and "smear sample" have all been used synonymously. For purposes of this section, the sample will be termed "wipe sample."

13.1.3 Applicability

This guideline is applicable when a sample of the substances on a surface is needed. Surfaces may include walls, floors, ceilings, desk tops, equipment, or other large objects that are potentially contaminated.

13.1.4 Responsibilities

The SM or designee is responsible for deciding when wipe sampling is needed.

Field personnel are responsible for performing the actual sampling, maintaining sample integrity, and preparing the proper chain-of-custody forms.

13.1.5 Records

Records of wipe sampling include completed chain-of-custody forms and appropriate entries in the field logbook. If the sample collected is to be analyzed using the National Contract Laboratory Program (CLP), then CLP forms must be completed as discussed in Section 5.

13.1.6 Procedures

Wipe sampling can be an integral part of the overall sampling program. Wipe sampling can help to provide a picture of contaminants that exist on the surface of drums, tanks, equipment, or buildings on a hazardous waste site or that exist in the homes of a populace at risk.

Wipe sampling consists of rubbing a moistened filter paper over a measured area of 100 cm^2 to 1 m^2. The paper is then sent to the laboratory for analysis. The results are related back to the known area of the sample. A proper sampling procedure is essential to ensure a representative, uncontaminated sample.

13.1.6.1 Equipment Required

The following equipment is needed for wipe sampling:

- Whatman 541 filter paper or equivalent, 15 cm
- Disposable, chemical-protective gloves
- Solvent to wet filter paper

13.1.6.2 Wipe Sampling Steps

The steps involved in obtaining a wipe sample are listed below:

- Using a clean, impervious disposable glove, such as a surgeon's glove, remove a filter paper from the box. (Note: Although it is necessary to change the glove if it touches the surface being wiped, a new glove should be used for each sample to avoid cross contamination of samples. A new glove should always be used when collecting a new sample.)
- Moisten the filter with a collection medium selected to dissolve the contaminants of concern as specified in the sampling plan. Typically, organic-free water or the solvent used in analysis is used. The filter should be wet but not dripping.
- Thoroughly wipe approximately 1 m^2 of the area with the moistened filter. Using a 1 m^2 stencil will help in judging the size of the wipe area. If a different size area is wiped, record the change in the field logbook. If the surface is not flat, be sure to wipe any crevices or depressions.

- Without allowing the filter to contact any other surface, fold it with the exposed side in, and then fold it over to form a 90-degree angle in the center of the filter.
- Place the filter (angle first) into a clean glass jar, replace the top, seal the jar according to quality assurance requirements, and send the sample to the appropriate laboratory.
- Prepare a blank by moistening a filter with the collection medium. Place the blank in a separate jar, and submit it with the other samples.
- Document the sample collection in the field logbook and on appropriate forms, and ship samples per procedures listed in Section 6.

13.1.7 Region-Specific Variances

No region-specific variances have been identified; however, all future variances will be incorporated in subsequent revision to this compendium. Information on variances may become dated rapidly. Thus, users should contact the regional EPA RPM for full details on current regional practices and requirements.

13.1.8 Information Sources

EBASCO. "Dioxin Sampling." *REM III Program Guidelines.* Prepared for U.S. Environmental Protection Agency. 28 February 1986.

NUS Corporation. "Site-Specific Site Operations Plans." REM/FIT Contract.

13.2 HUMAN HABITATION SAMPLING

13.2.1 Scope and Purpose

This subsection provides general guidance for the planning, method selection, and implementation of sampling activities used to determine the potential for human exposure to contaminants that are present in residential environment.

13.2.2 Definitions

Human Habitation Areas

Any place people may spend extended periods of time, such as their homes or offices.

13.2.3 Applicability

This subsection discusses sampling techniques that are similar in collection methodology to other types of samples, such as environmental soil and water, but are biased to emphasize potential human exposure to contaminants moving into the residential environment.

APPENDIX B8

PROCEDURE HGD-0009

GAS PHASE EXPLOSIVES TRAPPING EXPERIMENT

TENNESSEE VALLEY AUTHORITY

NO.: HGD-0009

TITLE: GAS PHASE EXPLOSIVES TRAPPING EXPERIMENT

Signature	Title	Date
Prepared by: Jon BA Wilson	Analytical Chemist	9/21/94
Concurred: William J. Rogers	QA Officer	9/21/94
Concurred: Kathleen C. Pugh	Research Chemist	9/21/94
Concurred:		
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Concurred:		
Approved: Joe J. Hoagland	Team Leader Specialist Analytical Laboratory	9/21/94

REVISION				
CONTROL DATE:				

COPY NO.: _____ HAS BEEN ISSUED TO HOLDER ON _____

TVA 17207 (OPM-8-83)

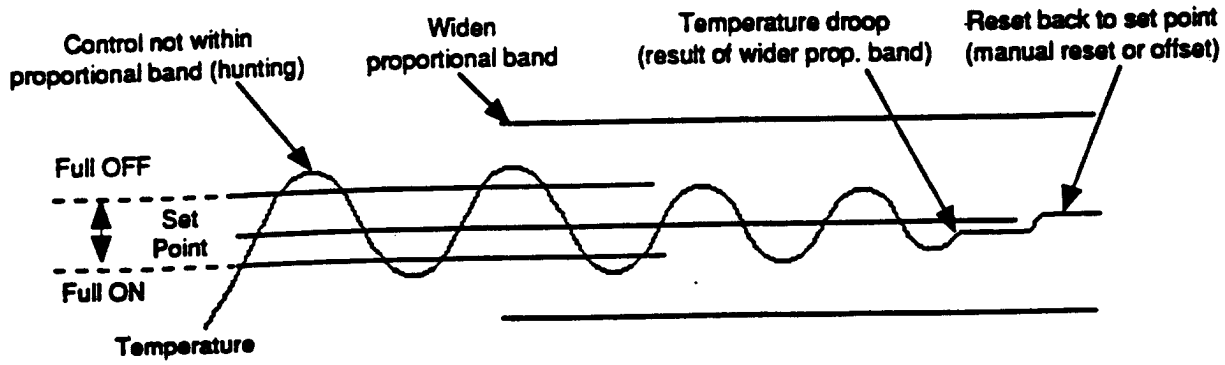

Figure 25 - Adjustment Graph

Tuning Procedure for Time Proportioning Controls w/Manual Reset

Initial Settings:
1. Proportional Band: Turn maximum clockwise; CW (widest setting)
2. Manual Reset: Turn to mid-range
3. Cycle Time: Turn maximum counterclockwise; CCW (fastest time)

Energize the system and allow the process temperature to stabilize. When the system is stable, the load light will cycle at a constant rate.

Proportional Band Adjustment:
Rotate the proportional band pot CCW 1/4 turn and observe system stability. Repeat until the process temperature begins to hunt (becomes unstable). When hunting is observed, rotate pot CW, in small increments, until the system becomes stable. Some systems may be stable enough to allow minimum proportional band setting (maximum CCW).

Manual Reset:
In virtually all proportional control systems the average process temperature may drop to a point that is not the set point temperature. This action takes place even though the process temperature has stabilized.

Monitor the actual process temperature on the digital indicator. Adjust the manual reset pot slowly CW if the process temperature stabilized below set point temperature. Adjust CCW if the process temperature stabilized above set point temperature. If large changes in set point temperature are made, readjustment of the manual reset may be required.

Cycle Time:
Set as required. Best control is always achieved with faster cycle times. However, if a mechanical contactor or solenoid is used to switch power to the load, slower cycle times may be desirable to minimize the wear on the mechanical components.

Cycle time pot is located internally on the bottom board, right side.

Tuning Procedure for ON/OFF Control w/Sensitivity and Offset

Initial Settings:
1. Switching sensitivity: Turn to mid-range
2. Offset: Turn to mid-range

Energize the system and allow to stabilize. When stable the load light cycles at a constant rate.

Switching Sensitivity Adjustment:
May be adjusted from 1°F/°C(CCW) to 5°F/°C(CW). Set the sensitivity adjustment maximum CCW if a narrow temperature differential is desired. Adjust the sensitivity maximum CW to increase the life of a mechanical contactor if the temperature differential is not critical.

Offset Adjustment:
Adjust the offset pot slowly CW until agreement is obtained if the average process temperature is lower than the set point temperature indicated on the display. Adjust the offset pot slowly CCW until agreement is obtained, if the average process temperature is above the set point temperature.

NOTE: Both pots are located internally on the bottom board, right side.

NOTE: For ease of adjusting, order extender board - Watlow P/N Z100-0421-0000.

I. TENAX-TA COLUMN

- Cut the glass tubing into approximately 7cm lengths (15 mm outside diameter 13 mm inside diameter).
- Plug the glass wool in the inlet of the column and pack the column from outlet side with Tenax-TA resin. (0.5-0.75 g).
- Plug the outlet side with glass wool.
- If there is going to be more than one section in the column, pack the Tenax-TA again and plug the end with glass wool.
- Condition the tube by connecting it to the combustion tube and running hot air through it. (Furnace at 300°C), for 1-24 hours.
- Place Parafilm on the inlet and outlet of the column if it is not going to be used immediately.

Set Up of Sample Train

- Connect the inlet of the Tenax-TA column with 2 inches of Tygon tubing to the end of the combustion tube.
- Connect the outlet of the column to the Tygon tubing leading to the gas impinger.
- Aliquot 100 ml of Acetonitrile into the gas impinger in series behind the column. Place it in an ice bath.
- Connect the outlet of the gas impinger to the Tygon tubing leading to the inlet of the thermocouple.
- Connect the outlet of the thermocouple holder to theTygon leading to the exhaust hood.
- The temperature of the thermocouple should be at or below room temperature before entering exhaust hood.

II. FURNACE PROCEDURE

- Set the desired temperature on the furnace with the setpoint knob.
- Set the proportional band to "maximize" (clockwise widest settings).
- Set the manual reset to "mid range."
- Turn on the power to the furnace to energize the system and allow the process temperature to stabilize. When the system is stable, the load light will cycle at a constant rate.
- Set the proportional band adjustment--Refer to Page 17 of Watlow Furnace Manual.
- Set the manual reset-refer to the attached page (no. 17) of theWatlow Furnace Manual.
- Unscrew the knob to the glass combustion tube. Place the quartz sample boat inside the combustion tube. Slowly push the container to the edge of the furnace (not in the furnace) with the sample introduction ladle.
- Turn on the U.P.C. air at the tank. (The flowmeter is set at approximately 965 ml/min.)
- Push the quartz sample container all the way into the furnace using the sample introduction ladle and magnet.
- Once the sample is introduced into the furnace, remove the sample introduction ladle with the magnet and replace the knob on the end of the combustion tube to re-establish a closed system.

- Turn off the lights in the lab and let the sample vaporize for one hour. Placard and lock the door.
- At the end of one hour, turn off the air at the gas cylinder.
- Turn the power switch on the furnace to "fan" and let the furnace cool down slowly. (When the temperature is less than 100 degrees centigrade, turn the power off.)
- Dismantle the column, combustion tube, Tygon joint connector, and gas impinger.

III. EXTRACTION

- Quantitatively transfer the contents of the column into a sample bottle along with the glass wool plugs. If the column is in two separate sections, place each section into separate sample bottles. Rinse the front end of the column into the sample bottle that holds the front section (if there is more than one section) with a known amount of acentonitrile.
- Rinse the combustion tube into a sample bottle with a known amount of acetonitrile.
- Rinse the Tygon joint connector into a sample bottle.
- Rinse the quartz sample boat into a sample bottle.
- Take an aliquot from the known volume of the gas impinger and transfer it to a sample bottle.
- Wrap all sample bottles tightly in foil to keep light out.
- Let the Tanax samples desorb in the Acentonitrile for approximately 30 minutes while slightly agitating every five minutes.
- Store sample in the refrigerator reserved for explosives experiment until analysis is scheduled.

APPENDIX C

LABORATORY CONTROL DOCUMENTS

LABORATORY CONTROL DOCUMENTS

C1 Procedure HGD-0001 - Spiking Explosives on Metal Surfaces

C3 Procedure HGD-0003 - Planning Samplnig Activities and Sampling

C4 Procedure HGD-0004 - Safety and Emergency Plans

C5 Procedure HGD-0005 - Use of Explosives Storage Room

C6 Procedure HGD-0006 - Method Detection Limits

APPENDIX C-1

PROCEDURE HGD-0001

SPIKING EXPLOSIVES ON METAL SURFACES

TENNESSEE VALLEY AUTHORITY

NO.: HGD-0001

TITLE: SPIKING EXPLOSIVES ON METAL SURFACES

Signature	Title	Date
Prepared by: William J. Rogers	QA Officer	10/26/94
Concurred:		
Concurred:		
Concurred:		
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Concurred:		
Approved: Joe J. Hoagland	Team Leader Specialist Analytical Laboratory	

REVISION	2			
CONTROL DATE:				

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TVA 17207 (OPM-8-83)

1.0 PURPOSE

This procedure describes those actions required to uniformly spike standard material on a metal surface or shell to similate uniform deposition of contaminants left after steam cleaning of the metal surface.

2.0 SCOPE

This procedure applies to work done in suport of the Hot Gas Decontamination Project at Hawthorne, Nevada.

It is followed by an extraction or smear procedure to test removal of the spiked compound for quantitative recovery. Alternately, it may be followed by other experimental activities such as heat treatment to remove spiked compounds.

3.0 SUMMARY

Three methods of spiking are described:

An explosive material is dissolved and allowed to run down the side of the shell.

An explosive material is placed in a shell with suitable solvent to make a solution.

An explosive material is dissolved and then deposited uniformly in a scribed area.

In each case, the solvent is allowed to evaporate, leaving a film of the material behind.

4.0 REFERENCES

4.1 "Dangerous Properties of Industrial Materials," Seventh Edition, N. Irving Sax and Richard J. Lewis, Sr., Van Nostrand Heinhold, New York

5.0 RESPONSIBILITIES

It is the reponsibility of the supervisor to ensure this procedure is followed and that employees utilize appropriate safety precautions. It is the responsibility of the supervisor to plan experiments and document required quantities and solvents.

It is the responsibility of the technician to follow this procedure, including the safety precautions. It is the responsibility of the technician to record all data and to report unusual results to the supervisor.

6.0 PROCEDURE/REQUIREMENTS

6.1 Prerequisites

6.1.1 Employees handling the quantities of explosive utilized in this procedure shall have had prior safety training in the handling of explosive materials.

6.1.2 Target compounds to be utilized, weights, volumes of solvent, and selection of solvent shall be selected prior to beginning manipulation of compound. Compounds selected, solvents selected, weights, volumes, additional experimental conditions, and any other pertinent data shall be recorded in a research notebook.

6.2 Limitations and Actions

6.2.1 The "Spike and Rinse" procedure steps may be utilized when an extremely large item is spiked which cannot be rotated easily.

6.2.2 The "*In-Situ* Dissolution" procedure steps may be used for moderate sized items which can be rotated or agitated. The purpose is to eliminate the need for multiple rinses of a weighing vessel and delivery device to ensure all the material is transferred.

6.2.3 The "Spiking a Scribed Area" procedure steps may be used when spiking items which are very large and cannot be moved at all or which will have access by a small port. It may also be used to spike small plates of metal which are tested by various extraction, washing, or heating processes for removal of material.

6.2.4 Weighings of target compounds should be made to 0.0001 g for total weights of less than 1 gram, to 0.001 g for total weights of less than 10 grams, and to 0.01 g for larger weights.

6.2.5 Evaporation of solvent is accelerated by inclining large shells so that the vapor, which is heavier than air, may flow out and down.

6.3 Requirements

6.3.1 Apparatus/Equipment

1-liter flask with ground glass stopper

1-liter Erlenmeyer flask

50-milliliter volumetric pipett

Analytical balance, calibrated, capable of weighing to 0.0001 g.

Laboratory balance, calibrated, capable of weighing to 0.001 g.

Technical balance, calibrated, capable of weighing to 0.01 g.

Face Shield

Gloves impermeable to the solvents.

Gloves resistent to heat for certain operations (target compound > 1 g)

Laboratory bench scale blast shield - transparent.

Teflon or metal plug machined to fit the test shell.

Non-sparking metal scribe

Area template (10 cm by 10 cm) or other size used to scribe an area to be spiked.

Glass dropper

Industrial roller tables, lifters, or other heavy manipulating equipment

6.3.2 Reagents and Standards

6.3.2.1 Acetone, HPLC grade

6.3.2.2 Acetonitrile, HPLC grade

6.3.2.4 Methanol, HPLC grade

6.3.2.5 Reagent grade water

6.3.2.6 Target compound (an explosive compound to be studied as provided by USAEC)

6.4 Calibration

The balances should be calibrated with traceability to the National Institute of Standards and Technology.

6.5 Procedure Instructions

CAUTION: Wear suitable gloves while performing the following steps. Avoid inhaling fumes. Work in an area with adequate ventilation. When spiking small components, work in a fume hood.

CAUTION: Wear eye protection to prevent splashes from getting in the eye.

CAUTION: The solvents are flammable and very volatile. Do not use near sources of heat, sparks, or ignition. Keep containers tightly closed when not in use.

CAUTION: In case of skin exposure, wash immediately with soap and water.

6.5.1 Spike and Rinse Process

6.5.1.1 Weigh a prescribed quantity of target compound into a flask as defined in the procedure planning step (see 6.1.2). Record the weight.

6.5.1.2 Add the solvent to fill approximately 90% of the volume of the flask. Stopper the flask and shake to dissolve. Invert periodically while shaking to ensure complete mixing.

6.5.1.3 Incline the shell to be spiked so that it is nearly horizontal.

6.5.1.4 Fill the pipette and allow the solution to drain down the side of the shell. If solution reaches the bottom of the object, reduce the angle of inclination so that it runs back on the side.

6.5.1.5 Allow the solvent to evaporate and form a thin film of the target compound on the side of the shell.

6.5.1.6 Rotate the shell so that a fresh surface is exposed and pipette more solution into it.

6.5.1.7 Repeat this until all the solution is used.

6.5.1.8 Rinse the flask with approximately 50 ml of solvent and pipette it onto the surface in a similar manner.

6.5.1.9 Repeat 6.5.1.8 with two more 50 ml portions of solvent.

6.5.2 *In-situ* Dissolution

6.5.2.1 Weigh a container plus the prescribed amount of the target compound. Record the weight.

6.5.2.2 Pour the target compound into the shell and weigh the empty container. Record the weight.

6.5.2.3 Add a suitable portion of solvent to the shell to dissolve the compound. Stopper the shell with a plug of appropriate size. Agitate the shell slightly to enhance dissolution.

6.5.2.4 Remove the plug and rinse the plug's surface which was exposed to the solution into the shell with two or three small portions of solvent.

6.5.2.5 Incline the shell to nearly horizontal and slowly rotate the shell to allow a thin film of solution to flow along the shell wall. Allow the solvent to evaporate while the shell is rotating to form a thin film of target compound on the wall of the shell.

6.5.3 Spiking a Scribed Area

6.5.3.1 Scribe a suitable area for testing (usually 100 square centimeters) with the non-sparking metal scribe. Utilize a template if one is available.

6.5.3.2 Weigh the target compound into the flask to the nearest 0.0001 g.

6.5.3.3 Add the smallest amount of solvent required to dissolve the compound.

6.5.3.3 Using a dropper, drop the solution into the scribed area and allow it to evaporate. Ensure the entire area is covered, but do not allow the solution to run outside the scribed area.

6.5.3.3 When all the solution is placed on the scribed area, rinse the flask and dropper three times with a small amount of solvent, dropping the rinsate into the scribed area as above.

6.6 Calculating and Reporting Data

Report weights utilized in spiking. When weights are calculated by difference, report initial and final weights and the difference.

7.0 QUALITY ASSURANCE PROVISIONS

7.1 Responsibility of Inspection

7.2 Acceptance Criteria

The dried material should be uniformly spread over the surface to be studied without visible bare patches, lumps, or accretions.

7.3 Material Monitoring

None

7.4 Equipment Monitoring

None

7.5 Certification

This procedure is certified by the review and approval process.

7.6 Quality Control Sample Requirements

None

8.0 SAFETY

8.1 Solvents utilized in this procedure have some hazards associated with them as summarized below. Also reference any Material Safety Data Sheets present in the work area.

8.1.1 Acetone is a flammable liquid. It is moderately toxic by various routes. It is a skin irritant and severe eye irritant. OSHA Permissible Exposure Limit is 1000 ppm. The Short Term Exposure Limit is 1000 ppm. It can react vigorously with oxidizing materials. It is commercially used as nail polish remover where its defatting action on skin is familiar.

8.1.2 Acetonitrile is a flammable liquid which is poisonous by ingestion and intraperitoneal routes. It is a skin and severe eye irritant. It is a dangerous fire hazard when exposed to heat, flame, or oxidizers. OSHA Permissible Exposure Limit is 40 ppm (70 mg/m^3). The Short Term Exposure Limit is 60 ppm.

8.1.3 Methanol is a flammable liquid which is poisonous by ingestion. Some experimental data show that it is poisonous by skin contact. It is mildly toxic by inhalation. Both by ingestion and inhalation it may attack the optic nerve. It is an eye and skin irritant. Death from ingestion of 30 ml has been reported. It is a dangerous fire hazard when exposed to heat, flame, or oxidizers.

8.1.4 They should be utilized in a laboratory hood for small objects and in a well ventilated area for large objects. A general rule of thumb is that if an odor is detected, the TLV has been violated. If an odor is detected, wear a respirator.

8.1.5 In case of skin contact, wash immediately with soap and water.

8.1.6 In case of eye contact, flush immediately with water, holding the eyes open to ensure they are rinsed.

8.2 Gloves impenetrable to the particular solvent must be worn when handling it. Gloves, safety glasses and lab coats shall be worn at all times while working with solutions. In addition, face shields shall be worn when working with dry compounds with quantities in excess of one gram.

8.3 The quantities of explosives utilized in this procedure are large enough quantities to constitute a hazard. No flames, sparks, or sparking materials shall be allowed in their presence. When working with the dry powders, electrical grounding shall be utilized to prevent sparks from static electricity. Avoid excess friction or impact.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICES

End of Document

APPENDIX C-3

PROCEDURE HGD-0003

"PLANNING SAMPLING ACTIVITIES AND SAMPLING"

TENNESSEE VALLEY AUTHORITY

NO.: FCD-0003

TITLE: PLANNING SAMPLING ACTIVITIES AND SAMPLING

Signature	Title	Date
Prepared by: William J. Rogers	QA Officer	10/2/84
Concurred:		
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Approved: Joe J. Hoagland	Team Leader Specialist Analytical Laboratory	

REVISION	1			
CONTROL DATE:				

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TVA 17207 (OPM-8-83)

1.0 PURPOSE

This document describes sampling activities for smears and projectiles extracts.

2.0 SCOPE

This document applies to field experiments in the Hot Gas Decontamination Project utilizing TVA personnel at Hawthorne, Nevada.

3.0 SUMMARY

Planning activities are described which document which samples to be taken and what solvents will be used.

Projectiles are sampled for spiked or residual explosives by solvent rinse or by smear with gauze material dampened with suitable solvent.

4.0 REFERENCES

None

5.0 RESPONSIBILITIES

It is the responsibility of the shift engineer to design the experiment, designate the number of samples to be taken, designate the sampling points, and to document experimental design.

It is the responsibility of the technician to follow this procedure and to adhere to all safety requirements.

6.0 PROCEDURE/REQUIREMENTS

6.1 Prerequisites

Procedure HGD-0001 - "Spiking Explosives on Metal Surfaces" will be used to spike the metal surfaces before extraction.

Procedure HGD-0007 - "EPA Wipe Sampling Technique" will be followed in performing wipe tests or smears.

6.2 Limitations and Actions

6.2.1 For extraction, the following solvents will be employed unless otherwise stated in the daily test plan.

Acetonitrile - Comp B, TNT, RDX, and HBX

Water - Yellow-D

50/50 mixture of Acetonitrile and Hexane - Comp A

6.2.2 Unless otherwise stated in the daily test plan designs, utilize the following quantities of solvent for extractions:

175 millimeter projectiles - 500 milliliters of solvent

5 inch and 106 millimeter projectiles - 100 milliliters of solvent

3 inch projectiles - 50 milliliters of solvent

6.2.3 Unless otherwise stated in the daily test plan designs, utlilize the following quantities of spike. Volumes of solvent suggested here are optional and may be changed in the field to optimize efficiency or to ensure the compound dissolves readily.

175 millimeter projectiles - 20 g target compound; usually dissolved in 100 ml solvent

5 inch projectiles - 7 g target compound; usually dissolved in 50 ml solvent

3 inch projectiles - 2.2 g target compound; usually dissolved in 25 ml solvent

6.3 Requirements

6.3.1 Apparatus/Equipment

Smears - Cotton cloth - sterile bandage quality.

Analytical Balance - Calibrated laboratory balance capable of weighing to 0.0001 g. Calibration traceable to National Institute of Standards and Technology.

Volumetric flasks - various sizes - laboratory grade.

Pipette - Type A volumetric - various sizes

Plug - a machined threaded plug designed to fit each type projectile.

Seals - adhesive paper seals used to seal sample bottles after sampling.

Custody Seal - A tamper-proof seal designed for chain of custody evidence.

Temperature Blank - a bottle filled with ethylene glycol or anitifreeze. Just before shipping, the temperature of this bottle is measured. Upon receipt, the temperature of this bottle will be measured. In this way, a thermometer need not be inserted in a sample.

6.3.2 Reagents and Standards

Water - HPLC grade

Acetonitrile - HPLC grade

Hexane - HPLC grade

50/50 mixture of acetonitrile and Hexane - mix equal volumes of HPLC grade acetonitrile and hexane.

50/50 mixture of acetione and water - mix equal volumes of HPLC grade acetone and water.

Target compound - an explosive compound supplied at Hawthorne

50 ppm standard. Weigh approximately 50 mg of target compound into a tared 1-liter volumetric flask. More than one compound may be utilized. Bring to the mark with a suitable solvent such as water or acetonitrile. Other concentrations may be prepared in like manner if experimental design calls for them.

5 ppm standard. - Dilute 25 ml of the 50 ppm standard to 250 ml in a volumetric flask. Other concentrations or volumes may be made in like manner if experimental design calls for them.

Ethylene glycol - commerical antifreeze or reagent grade ethylene glycol used as a temperature blank.

6.4 Calibration

None

6.5 Procedure Instructions

6.5.1 - Devising and Documenting a Sampling Plan

For each facility load, select one spiked item at random to be extracted before the run. (The purpose of this sample is to verify spiking before the run). Note the location of the other spiked surfaces or projectiles. Ensure they are marked so they can be relocated. Note their location on the Sampling Workplan. Document the date, time, projectile type, constraints of the run, and other pertinent information on the Workplan. Attach any pertinent drawings for reference. Note any special sampling constraints such as duplicate samples, multiple smears in the same spot, special techniques, whether multiple smears should be separated or placed in the same bottle, etc.

6.5.2 - Spiking

Dissolve the correct quantity of target compound as listed in sections 6.2.1 and 6.2.3 above. Follow HGD-0001 for spiking instructions. Record all quantities and actions in a field logbook.

6.5.2 - Extract Sampling

Complete a Field Sampling Sheet utlizing the information on the Sampling Workplan

Place a suitable quantity of solvent into the projectile to be extracted. Stopper the projectile with a plug.

Rotate and agitate the projectile for the time prescribed on the field sheet. Mechanical shakers, rolling machines, or other aids may be used to rotate or agitate the projectile.

Label the sample container.

Remove the plug and rotate the projectile so that the solvent will drain. Collect the solvent in the sample container. For multiple extraction experiments, catch as much as possible and allow the surface to drain completely before introducing more solvent.

Log times, solvents, quantities used, and an estimate of the quantity recovered on the field sheet.

Seal the bottle.

Repeat for the number of times prescribed in the field sheet. (Usually single extraction only.)

6.5.3 - Making Standard Solutions

The 50 ppm standard solution and the 5 ppm standard solution shall be made in accordance with the mixing instructions above. All weights and volumes shall be recorded on a Solution Logsheet

6.5.4 - Addition of Quality Control Samples to Sampling Lot

Once an extraction sampling lot is assembled, add a blank, a 50 ppm standard, and a 5 ppm standard solution for each group of 20 samples or subset thereof. Utilize volumes of the blank and standards similar to the volume of the lot. Utilize the same type bottles, labels, seal, and pen as for the field samples. Also include a labeled bottle with a portion of the spiking solution for verification.

For a smear sampling lot, add a blank smear a 50 ppm standard and a 5 ppm standard for each 20 samples or subset thereof. Seal these samples in labeled bottles just as would be done for routine samples. Record the quantity of 50 ppm standard which was used on the Solution Logsheet.

6.5.5 - Numbering of Samples

Samples should be assigned numbers on a systematic basis. The 10-ml spiking solution sample and other known high-concentration samples should be clearly labeled for what they are.

6.5.6 Chain of Custody Papers and Shipment

Arrange the samples in numerical order. Complete the "Chain of Custody" form. Double-check the form for accuracy. Sign and date the "Relinquished by" portion of the form. Pack the samples in plactic bags and then in a cooler filled with ice. Add a temperature blank. Note the temperature on the custody form. Seal the cooler with a custody seal. Attach a copy of the chain of custody papers to the outside of the cooler. Fax a copy to the receiving laboratory. Contact the shipping company and arrange pickup.

6.5.1 - Smear Sampling

(Note: in the following section , it may be helpful to complete as much of the field sheets and labels as is known beforehand.)

Complete a Field Sampling Sheet utlizing the information on the Sampling Workplan

Label a sample bottle with an identifying number or code from the worksheet.

Wear gloves. Change them for each smear location, if contamination of the gloves is suspected, or if solvent breakthrough is expected.

Moisten a smear with a suitable solvent. Holding the smear in in gloved hand or extension probe, vigorously scour the scribed area with the moist smear. Immediately place it into the sample bottle. Rinse the tongs to prevent contamination of the next sample. If the sampling plan requires it, repeat with another smear and place it in the same bottle. Usually, only single smears are planned.

Log all actions, locations, solvent, and number of smears on the Sampling Field Sheet.

Seal the bottle.

6.6 Calculating and Reporting Data

None

7.0 QUALITY ASSURANCE PROVISIONS

7.1 Responsibility of Inspection

It is the responsibility of the engineer to ensure sampling plans are complete and reasonable.
It is the responsibility of the technician to ensure sample documentation is complete, random numbers are assigned without duplication, and that the chain of custody form is correctly completed.

It is the responsibility of the technician to ensure sample documentation is complete, random numbers are assigned without duplication, samples are taken in accordance with the sampling plan, and that the chain of custody form is correctly completed.

7.2 Acceptance Criteria

The chain of custody form must be completely filled out. All blanks must be completed or a line and "NA" drawn through them. All samples listed on the form must be sealed in the cooler with no extra samples and no omissions.

The cooler must be correctly sealed with evidence tape with no breaks or tears.

7.3 Material Monitoring

None

7.4 Eqiupment Monitoring

None

7.5 Certification

This procedure is certified by the review and approval process.

7.6 Quality Control Sample Requirements

None

8.0 SAFETY

8.1 Solvents utilized in this procedure have some hazards associated with them as summarized below. Also reference any Material Safety Data Sheets present in the work area.

8.1.2 Acetonitrile is a flammable liquid which is poisonous by ingestion and intraperitoneal routes. It is a skin and severe eye irritant. It is a dangerous fire hazard when exposed to heat, flame, or oxidizers. It reacts with water. OSHA Permissible Exposure Limit is 40 ppm (70 mg/m^3). The Short Term Exposure Limit is 60 ppm.

8.1.3 Methanol is a flammable liquid which is poisonous by ingestion. Some experimental data show that it is poisonous by skin contact. It is mildly toxic by inhalation. Both by ingestion and inhalation it may attack the optic nerve. It is an eye and skin irritant. Death from ingestion of 30 ml has been reported. It is a dangerous fire hazard when exposed to heat, flame, or oxidizers.

8.1.4 The solvents should be utilized in a laboratory hood for small objects and in a well ventilated area for large objects. A general rule of thumb is that if an odor is detected, the TLV has been violated. If an odor is detected, wear a respirator.

8.1.5 In case of skin contact, wash immediately with soap and water.

8.1.6 In case of eye contact, flush immediately with water, holding the eyes open to ensure they are rinsed.

8.2 Gloves impenatrable to the particular solvent must be worn when handling it.

8.3 The quantities of explosives utilized in this procedure are large enough to constitute a hazard. No flames, sparks, or sparking materials shall be allowed in their presence. When working with the dry powders, electrical grounding shall be utilized to prevent sparks from static electricity. Avoid excess friction or impact.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICES

END OF PROCEDURE

Field Sampling Sheet
Solvent Extractions

Sheet No: _____

Solvent: _____ Volume: _____

Date YY-MM-DD	Random Number	Sample Description
_____	xxx	Spiking Solution - 10 ml
_____	_____	Blank
_____	_____	High QC Reference
_____	_____	Low QC Reference
_____	_____	1
_____	_____	2
_____	_____	3
_____	_____	4
_____	_____	5
_____	_____	6
_____	_____	7
_____	_____	8
_____	_____	9
_____	_____	10
_____	_____	11
_____	_____	12
_____	_____	13
_____	_____	14
_____	_____	15
_____	_____	16
_____	_____	17
_____	_____	18
_____	_____	19
_____	_____	20
_____	_____	Blank
_____	_____	High QC Reference
_____	_____	Low QC Reference
_____	_____	21
_____	_____	22
_____	_____	23
_____	_____	24
_____	_____	25
_____	_____	26
_____	_____	27
_____	_____	28
_____	_____	29
_____	_____	30
_____	_____	31
_____	_____	32
_____	_____	33
_____	_____	34
_____	_____	35
_____	_____	36
_____	_____	37
_____	_____	38
_____	_____	39
_____	_____	40

Reference Planning Sheet Number _____

Notes

Signature: _____

ampling Workplan Sheet Number _____

Scheduled Date: _____

Description of Experiment Solvent: _____

Total number of samples _____

Sampling Locations

1	11	21	31
2	12	22	32
3	13	23	33
4	14	24	34
5	15	25	35
6	16	26	36
7	17	27	37
8	18	28	38
9	19	29	39
10	20	30	40

Additional Information

Signature: _____

Solution Logsheet: Sheet Number: _____

Stock Solutions - Makeup

Compound	Mg	Total Volume	Solvent	Name	Date	ID Number	Conc.

Dilution of Stock Solutions

ID Number Stock	Ml Used	Total Volume	Solvent	Name	Date	ID Number Dilution	Conc.

Use of solutions to make QC samples

ID Number	Ml Used	Sample ID	Name	Date	Total Mg

CHAIN OF CUS Y RECORD
RCRA FACILIT STIGATION
TVA-National Fertilizer & E mental Research Center
Muscle Shoals, Alabama 35660

SWMU No.	SWMU Name

Samplers *(Signature)*

Sample No.	Date	Time	Comp.	Grab	Sample Location	No. of Containers											Remarks

Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date Time	Received for Laboratory by: *(Signature)*		Remarks	

TVA 29203 (RD-NFE-4-90)

Copy 1 - Field Investigator
Copy 2 - Field Investigator
Copy 3 - Retained by Laboratory

1

APPENDIX C-4

PROCEDURE HGD-0004

"SAFETY AND EMERGENCY PLANS"

TENNESSEE VALLEY AUTHORITY

NO.: HGD-0004

TITLE: "SAFETY AND EMERGENCY PLANS"

Signature	Title	Date
Prepared by: William J. Rogers	QA Officer	7/27/94
Concurred: Kathleen C. Pugh	Analytical Chemist	7-27-94
Concurred:		
Concurred:		
Concurred:		
Concurred:		
Approved: Joe J. Hoagland	Team Leader Specialist Analytical Laboratory	8/2/94

REVISION				
CONTROL DATE:				

COPY NO.: _____ HAS BEEN ISSUED TO HOLDER ON _____

TVA 17207 (OPM-8-83)

1.0 PURPOSE

This document describes safety requirements and emergency plans for the Hot Gas Decontamination Project at TVA's Environmental Research Center. See Note 7.1.

This document is not intended to restate all existing safety requirements in place for TVA laboratories, but is intended to describe those additional requirements specific to this project.

2.0 SCOPE

This document applies to work performed at TVA's Environmental Research Center in support of the Hot Gas Decontamination Project. This work will involve experiments and measurements with small quantities of high explosives.

3.0 SUMMARY

In addition to existing TVA safety requirements and existing emergency plans, additional detailed requirements are specified.

4.0 REFERENCES

4.1 "Manual of Safe Work Practices," October 1990, Resource Development, Tennessee Valley Authority

4.2 "Chemical Hygiene Plan", National Fertilizer and Environmental Research Center, Revision 1, Issued November 26, 1991

4.2.1 Appendix I to the "Chemical Hygiene Plan", "Emergency Plan"

4.3 "Quality Assurance Plan," QA-PLAN, Revision R1, Chemical and Environmental Analysis Section, Tennessee Valley Authority, February 18 10, 1993.

4.4 "Control of Reagents and Standards," GLP-0006, Revisions R0, General Analytical Laboratory, Tennessee Valley Authority, September 28, 1989.

5.0 SAFETY REQUIREMENTS

The general laboratory safety requirements of references 4.1 and 4.2 apply with the following additions:

5.1 Defined Work Areas - Work with explosive target compounds for the Hot Gas Decontamination Project shall be limited to the following locations:

- Weighing and desiccating target compounds in room L171 -172 (< 1 g).
- Storing and weighing larger quantities (> 1 g) of target compounds in room T5.
- Mixing standard solutions, making dilutions, and performing initial sample preparation in room L171-172 and room L265-266.
- Performing liquid chromatography concentration measurements on samples stored in an autosampler tray in room L173 - 176 and L265 - 266.
- Performing spiking, smearing, and extraction experiments in room L171 - 172.
- Volatilization of test amounts of target compounds in a tube furnace and collecting them in a sampling train in room L170.

5.2 Occupancy of Work Areas -

5.2.1 An analytical area is defined as a ten foot radius around a work area within the same room. Occupancy of analytical areas shall be limited to the following:

- Weighing of standards - one operator and one backup.
- Mixing of standards - one operator and one backup.
- Dilution of solutions, loading of sample vials, sample preparation - one operator and no more than one other person in room L171 - 172 and no more than three other persons in room L173 - 176 and L265 - 266.

5.2.2 Occupancy of the tube furnace area shall be one person while the furnace is loaded or unloaded. Ordinarily, the room should be evacuated, locked, and placarded when the experiment is running.

5.3 General Safety

5.3.1 As required by the QA Plan (ref. 4.3), all work carried out under this project shall be performed in accordance with written, approved procedures.

5.3.2 Gloves, safety glasses and lab coats shall be worn at all times while working with solutions. In addition, face shields shall be worn when working with dry compounds with quantities in excess of one gram.

5.3.3 Aisles, doorways, and hallways shall be kept clear to allow for instant exit.

5.3.4 Avoid mechanical shock, flame, sparks, static electricity when working with dry compounds. Work on grounding mats when working with dry compounds. Avoid flame and sparks when working with solutions.

5.3.5 Dry compounds and solutions shall be stored as close to the floor as possible in their respective storage locations.

5.3.6 Solutions and compounds shall be stored and transported in secondary containment (for example: plastic trays or pans) to limit spills.

5.3.7 Inspect storage container threads and frits for dried target compound. Clean threads and frits to prevent any buildup which might detonate due to friction in opening or closing the containers.

5.3.8 When weighing dry target compounds do not use plastic spatulas and weighing dishes. Use metal spatulas and metal weighing dishes instead.

5.3.9 Refrigerators in L171 - 172 used in storing solutions or dry target compound shall be rated as explosion proof. The refrigerators shall be locked when not being accessed.

5.3.10 Each experiment or procedure step requiring the use of dry target compound should be designed to use the smallest quantity of material practicable.

5.3.11 Rooms containing target compounds shall be placarded. They shall be locked after hours to prevent accidental contact with the compounds.

5.3.12 Placards for rooms shall state "Explosives - Unauthorized Entry Strictly Prohibited." Placards for equipment such as refrigrerators shall state "Explosives - Unauthorized Access Strictly Prohibited." Placards for rooms shall have names and phone numbers for emergency contacts which include the Team Leader and Materials Cusodians.

5.4 Storage of Materials

5.4.1 Dry compounds shall be partitioned into approximately one gram quantities and stored in separate containers, each appropriately labeled. These containers shall be stored in spacers or racks which place them at least one inch apart.

5.4.2 Dry standard materials shall be stored in an explosion-proof container in the storage room (T5). The room shall be kept locked with three persons having key custody, the materials custodians. All access to the room shall be logged. (See form 8.1) A copy of the key shall be maintained with TVA Public Safety with appropriate security controls. All access to the room to use the compounds shall be made by a materials custodian accompanied by a backup who does not enter the room but remains outside to call for help should an incident occur.

- Exception: Small quantities of standard material which are required to be stored in a refrigerator shall be stored in the explosion-proof refrigerator in L171-172.

- Exception: Small quantities of standard material which are required to be stored in a desiccator shall be stored in L171-172.

5.4.3 Only the quantity of material to be used should be removed from the storage room. It should be weighed into a container and the original container replaced in the storage container.

- Exception: If in certain experiments, entire one-gram containers of dry standard materials need to be removed from T5, they shall be removed for only the length of time required to utilize them in making standards or performing experiments. They shall be kept under lock and key while not being directly utilized in the laboratory and shall be returned to T5 as soon as practicable.

5.5 Storage of Solutions - Solutions made from standard material shall be stored in an explosion-proof refrigerator in room L171 - 172. The room shall be locked at night and during the day when unattended to prevent accidental contact with the solutions. The refrigerator shall be placarded to warn of the presence of explosive compounds. Solutions with total concentration of target compounds greater than 1% (10,000 ppm) shall be stored in the refrigerated sample storage room T11.

5.6 Labeling Solutions - Solutions shall be labeled with the compounds present, concentration, and solvent in accordance with the requirements of the QA Plan (ref. 4.3) and GLP-0006 (ref. 4.4). Dry compound containers shall be labeled in accordance with the same requirements.

5.7 Tube Furnace Experiments

5.7.1 While performing tube furnace experiments, doors shall be placarded to prevent accidental access. The door shall not be blocked, however.

5.7.2 Blast shields shall be used in tube furnace experiments.

5.7.3 Quantities of target compounds shall be limited to 200 milligrams in tube furnace experiments. Smaller quantities should be used when practical.

5.7.4 Tube furnace experiments shall be temperature controlled to ensure a long heating time with continued gas flow to drive volatilized compound into the sampling train. At no time should rapid heat be applied which might result in a detonation.

5.7.5 Following tube furnace runs, joints and cool spots shall be visually inspected for condensation of target compound. After experimental runs, the interior surface of the exposed components shall be triple-rinsed with a suitable solvent to ensure contamination or residues are eliminated.

5.8 Sample Storage and Transport

5.8.1 Samples shall be stored in a refrigerated storage room located in either T11 or T5. If after analysis solutions are found to contain more than one percent of target compound, they shall be moved to T11 pending proper disposal.

5.8.2 Samples shall be stored in plastic trays or pans to prevent dropping and spilling.

5.8.3 Samples shall be transported between rooms in plastic trays or pans or in rubber buckets.

5.8.4 Samples shall be returned to the storage area as soon as practical after use.

5.9 Liquid Waste

5.9.1 Liquid waste should be segregated by target compound insofar as that is possible. Waste containers should be no larger than five gallons. Full waste containers should be analyzed for disposal as soon as practical. Pending disposal, waste shall be labeled and stored in the sample storage area in plastic pans or trays (or secondary containment).

5.9.2 Waste containers may be stored in the laboratory while operations are in progress, but should be properly labeled.

5.9.3 Full waste containers should not be left in the laboratory overnight with the exception of the liquid chromatograph discharge stream during automated runs. This discharge container shall be kept in a plastic tray or pan to catch overflows or spills.

5.9.4 Labels of waste containers shall contain the words "HPLC Effluent," the name of the solvent or solvents, and the compounds expected to be present.

5.10 Solid Waste

5.10.1 Solid waste known to be contaminated shall be stored in plastic bags with labels in either T11 or T5 pending shipment to Hawthorne for disposal.

5.10.2 Solid waste suspected to be contaminated may be accumulated in the laboratory work area in plastic bags. When bags are full, they shall be stored as in 5.10.1

5.11 Definition of Clean Glassware

Glassware may be considered clean after draining, triple rinsing with a suitable organic solvent, and then washing with soap and water. Collect the organic rinses and treat them as liquid waste as in 5.9.

5.12 Chemical Hygiene Committee Review

This Safety and Emergency Plan and the work under its scope shall receive a hazard review by the Chemical Hygiene Committee of Analytical Support Services as specified in the Chemical Hygiene Plan (ref. 4.2) . Changes in quantities utilized in experiments shall be reviewed as specified by the Chemical Hygiene Plan.

6.0 EMERGENCY PLAN

The requirements of reference 4.2.1 apply with the following additions specific to this project.

6.1 Cooling loss

No cooling lines are proposed in the experimental setup.

6.2 Vacuum loss

If vacuum is used to move the gas stream through the tube furnace, vacuum failure should be followed by immediate shutdown of the furnace power supply.

6.3 Power loss

If power loss occurs due to line failure, disconnect or shut down equipment so that it does not come back on unexpectedly.

Power loss in tube furnace experiments is not expected to provide additional hazards although deposition of target compound can occur on interior surfaces. In this case, the furnace should be disassembled and cleaned with a suitable solvent.

Power loss in liquid chromatographs could result in deposit or condensation of target compounds in interior sample pathways. The unit should be cleaned by injecting solvent until a good baseline is observed unless chromatogram traces indicate no appreciable amount of target compound was present in the machine at the time of power failure.

6.4 Spills

6.4.1 Liquid Spills of Organic Solvents Such as Acetone, Ethanol, Methanol, and Acetonitrile

6.4.1.1 Spills should be contained in the secondary containment described throughout section 5 above.

6.4.1.2 Small spills that miss containment should be cleaned up by paper towels. Place contaminated towels in a plastic bag in a hood while cleanup work is in progress.

6.4.1.3 Spills larger than 500 ml should be cleaned up with an organic spill kit while wearing a respirator. The kits are located on the carts near the stairwell. Respirators must be individually fit tested and the wearer must have passed a medical examination.

6.4.1.4 Dispose of paper towels and solid waste as described in section 5.10.

6.4.2 Solid spills

Since quantities of target compound are limited to 1 gram or less, clean spills of solid material by sweeping gently with a paper towel into a plastic bag. Follow this by cleaning the surface with soap and water. Dispose of solid waste as in section 5. For larger spills, contact the hazard response team for the building.

6.5 Hood failure

Halt any reaction or operation occurring in the hood. Cap containers. Leave the work area and notify the supervisor and Chemical Hygiene Officer. Lock the room to prevent unauthorized entrance. Clear the hood of hazards before repair personnel begin work where they might come in contact with them. After repair, ensure the hood is operational before starting operations in it.

6.6 Fire

Leave the work area. Notify Public Safety. Pull the local fire alarm. Notify the supervisor.

6.7 Explosion

Leave the work area. Notify Public Safety. Pull the local fire alarm. Notify the supervisor.

6.8 Accidental Personal Exposure

Wash the exposed area immediately with soap and warm water. If eyes are exposed, call loudly for help and use the nearest eye wash. If large areas are exposed, utilize the nearest

safety shower. Follow this by a shower with soap and warm water. If clothing is contaminated, remove it immediately and do not replace it until after it is laundered.

6.9 Runaway Reactions

Leave the work area. Notify Public Safety. Notify the supervisor.

6.10 Emergency Shutdown Procedures

To shut down the tube furnace assembly, disconnect the power.

To shut down the liquid chromatograph, turn off the uninterruptible power supply connected to the unit.

6.11 Unrelated Building Emergencies

If in the course of analysis or experiments an unrelated building emergency occurs such as a fire drill, tornado warning or the like which requires evacuation of the workspace

- Disconnect power for any activity which would cause a hazard if power failed and came back on. (Example: Tube furnace experiment)
- Evacuate the area as instructed.

6.11 Notifications

Following any incidents listed above, the supervisor should be notified. Do not delay in obtaining medical help or emergency response in order to find the supervisor first. Likewise, notify the Chemical Hygiene Officer and the Team Leader of Support Services.

7.0 NOTES

7.1 The compounds utilized in this project in the quantities proposed and under routine laboratory handling conditions may be safely weighed, dissolved, and analyzed. The intent of this document is to provide an additional margin of safety to ensure there is no explosion or fire. Quantities are limited to provide even greater margin of safety so that if there were an explosion, its effects would be minimized.

END OF DOCUMENT

APPENDIX C-5

PROCEDURE HGD-0005

"USE OF EXPLOSIVES STORAGE ROOM"

TENNESSEE VALLEY AUTHORITY

NO.: HGD-0005

TITLE: USE OF EXPLOSIVES STORAGE ROOM

Signature	Title	Date
Prepared by: William J. Rogers	QA Officer	5/25/94
Concurred: Kathleen C. Pugh	Research Chemist	7/19/94
Concurred:		
Concurred:		
Concurred:		
Concurred:		
Approved: Joe J. Hoagland	Team Leader Specialist Analytical Laboratory	7/14/94

REVISION	R0	R1		
CONTROL DATE:	5/25/94			

COPY NO.: _____ HAS BEEN ISSUED TO HOLDER ON _____

TVA 17207 (OPM-8-83)

1.0 PURPOSE

This procedure gives the protocols and controls for entry to the explosives storage room (T5) and for use of the compounds stored there.

2.0 SCOPE

This applies to entry to the explosives storage room in T5 and to access to the explosives storage container.

3.0 SUMMARY

Entry to the storage room is logged. Safety controls are specified. Use or removal of the dry solids stored there is logged.

4.0 REFERENCES

4.1 HGD-0004 "Safety and Emergency Plans", Tennessee Valley Authority, Analytical Laboratory, Support Services, Environmental Research Center, Muscle Shoals, Alabama

4.2 CP-0001, "Measuement and Test Equipment Control and Calibration," Tennessee Valley Authority, Chemical and Environmental Analysis Section, Revision R2, September 20, 1993.

5.0 RESPONSIBILITIES

5.1 It is the reponsibility of the person performing this procedure to adhere to the safety requirements herein, to document all access to the room, and to document all use of the target compounds stored in the room.

5.2 It is the reponsibility of the Team Leader, Analytical Laboratory Support Services to ensure this procedure is followed. It is the repsponsibility of the Team Leader to appoint materials custodians.

6.0 PROCEDURE/REQUIREMENTS

6.1 Prerequisites

6.1.1 The Team Leader shall appoint three persons in the organization to be materials custodians. These individuals shall have copies of the keys to the room and to to padlock on the storage container. Another key set shall be maintained with Public Safety. The Team Leader shall have a fifth key set.

6.1.2 The materials custodian performing this procedure must be thoroughly familiar with the safety requirements of HGD-0004.

6.1.3 Public Safety shall be instructed to not allow access to the storage room in case of fire. The storage container is designed to withstand any explosion which might occur.

6.1.4 Public Safety shall be instructed to communicate any use of the keys controlled by them to Joe Hoagland.

6.1.5 Materials custodians shall have been trained in General Explosives Safety, in the contents of HGD-0004, and in the contents of this Procedure. This training shall be documented.

6.2 Limitations and Actions

6.2.1 The explosive storage room and the steel container in it are to be used to store dry target compounds which are not being used directly in experiments. Those dry compounds, usually standard materials, which must be refrigerated may be stored elsewhere as described in HGD-0004. Small quantities (less than one gram) which must be desiccated at all times may be stored elsewhere as described in HGD-0004.

6.2.2 All the requirements of HGD-0004 apply to this procedure.

6.2.3 In the event of the absence of the materials custodians, the Team Leader, ALSS may assign another individual who has had the proper training and is thoroughly familiar with HGD-0004 and this procedure to perform the work herein.

6.2.4 The emergency backup person shall have been trained in the contents of this procedure before serving in that capacity.

6.2.5 This procedure and HGD-0004 are written to allow up to fifty grams of explosive material to be stored in the storage room. If that amount is to be exceeded, this procedure and HGD-0004 must be reviewed and modified as necessary.

6.2.6 A lab coat, gloves, and a face shield are required for opening and use of the storage container.

6.2.7 Access to the room for other purposes than to open the explosives storage container and to work with the compounds stored in it is permitted. This access need not be by the materials custodian, but must be logged. An example of this access would be the routine monthly balance check.

6.3 Requirements

6.3.1 Apparatus/Equipment

6.3.1.1 Explosives storage container - a steel container, painted red, labeled with the word "Explosives". This container must have no source of heat, flame, or sparks. The container shall be padlocked when not being accessed.

6.3.1.2 Analytical balance - a balance capable of weighing to 0.1 mg with calibration traceable to the National Institute of Standards and Technology.

6.3.1.3 Logbook - A bound logbook with sequentially numbered pages. The logbook shall have carbon paper or another means of duplicating each page as it is written. Completed pages shall be removed and stored separately. The logbook shall be stored in room T5 until the project is complete. Pages of the logbook shall be designed to list all the bottles of target compound stored in the room and their use. Complete traceability of each use of the compounds and ultimate disposal shall be provided.

6.3.1.4 Inventory Cards - Should the inventory increase to the size that a logbook cannot be readily used to provide traceability, an inventory card system shall be utilized which provides information on each bottle of compound including source, identification code, use, quantity, dates, and ultimate disposal. References below to "logbook" for inventory control may be understood to apply to inventory cards. Inventory cards may be stored outside the room for safekeeping, but should be carried into the room so that data may be written directly on them rather than on another piece of paper and then transferred.

6.3.2 Reagents and Standards

6.3.2.1 Target Compounds - An explosive compound or byproduct to be studied as provided by USAEC.

6.4 Calibration

None

6.5 Procedure Instructions

6.5.1 Key Control

6.5.1.1 The materials custodians will keep one copy of the key to the room and the key to the padlock on his or her person. The key will not be kept locked in a desk. Transfer of the keys and custody shall be done by the Team Leader. Any transfer of reponsibility shall be logged in the explosives room logbook. The keys shall never be left unattended.

6.5.1.2 A set of keys shall be kept with Public Safety. The keys shall have a tag attached which clearly states "Explosives Storage Room - Limited Access." Any access to this key shall be logged with public safety.

6.5.1.3 A set of keys shall be assigned to the Team Leader. These keys may be kept locked in a secure place or may be kept on his person. The keys shall never be left unattended.

6.5.2 Addition of New Compounds to the Storage Area

Partition the newly received compound into approximately one gram quantities in suitable containers for storage. Label each bottle with a unique identifier and log the numbers in the logbook. Place the bottles in a rack with approximately one inch space between each bottle. Place the rack in the explosive storage container.

6.5.3 Room Access

6.5.3.1 As required in HGD-0004, only one person enters T5 to open and access the storage container. This must be a materials custodian. Another person, the emergency backup, shall remain present outside the storage area to call for help in the event of an incident. This second person may be any employee who is suitably trained. The emergency backup stays in the hallway outside the room and away from the door so as to avoid flying glass in event of an accident. See attachment 1.

6.5.3.2 All entry into the room must be logged in the explosives room logbook. The date, time, person's name, and reason shall be logged.

6.5.4 Use of Compounds

6.5.4.1 Handling of compounds in the storage room should be limited to weighing the compound into a container which will then be removed from the room.

6.5.4.2 Weigh the compound. Log the weights, identification numbers, proposed use of the compound and other pertinent data.

6.5.5 Removal of Compounds

6.5.5.1 In the case that a storage container for a compound must be removed from the storage room for an experiment, the action and its reason shall be logged. Estimated quantity to be used shall also be logged.

6.5.5.2 Transport the container singly in a plastic pan or bucket to the location for the experiment.

6.5.5.3 While utilizing the compound in an experiment, do not leave it unattended. Store the bottle under lock and key if it is to be left in the room for the experiment. Return the bottle to the storage container as soon as possible. Never leave the bottle outside the storage container overnight.

6.5.5.4 When the bottle is returned to the storage room, log its return. Log the amount actually used and its purpose. If the compound was used up in the experiment, log this in the logbook as well.

6.6 Calculating and Reporting Data

None

7.0 QUALITY ASSURANCE PROVISIONS

7.1 Responsibility of Inspection

Is the responsibility of the group leader to inspect logs and records to ensure they are accurate and complete.

It is the responsibility of the Quality Assurance Officer to perform inspections of the records produced in the performance of this procedure.

7.2 Acceptance Criteria

All access to the room and actions involving use of the materials shall be logged. Data shall be logged in enough detail to reconstruct any use of the compounds. Inventory records shall completely describe each bottle of compound.

7.3 Material Monitoring

None

7.4 Eqiupment Monitoring

Balances are monitored in accordance with procedure CP-0001.

7.5 Certification

This procedure is certified by performing a walk-through using an inert compound.

7.6 Quality Control Sample Requirements

None

8.0 SAFETY

Safety requirements are specified in detail in HGD-0004.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICES

Attachment 1 - Instructions for Backup

Instructions for Emergency Backup - Access to Storage Room

1. Remain in hallway away from the door while the materials custodian works in T5. The door should be blocked open or unlocked during use.
2. Should an emergency occur, call Public Safety at **8911** or **2444**

The nearest telephone will be in one of the offices in the main hallway.

3. Provide any immediate assistance needed by the person in T5 including help using the safety eye wash. Assist them holding their eyes open and call loudly for help.
4. Other Phone Numbers

Team Leader - Joe Hoagland - 2108
Chemical Hygiene Officer - Bill Rogers - 3744
Materials Custodian - David Phillips - 3358
Materials Custodian - Jon Wilson - 2644
Materials Custodian - Amanda Gordon - 2460
Grop Secretary - Kathy Ford - 2186

END OF PROCEDURE

APPENDIX C-6

PROCEDURE HGD-0006

"METHOD DETECTION LIMITS"

TENNESSEE VALLEY AUTHORITY

NO.: HGD-0006

TITLE: METHOD DETECTION LIMITS

Signature	Title	Date
Prepared by: William J. Rogers	QA Officer	5/17/94
Concurred: Kathleen C. Pugh	Analytical Chemist	7/19/94
Concurred:		
Concurred:		
Concurred:		
Concurred:		
Approved: Joe J. Hoagland	Team Leader Specialist Analytical Laboratory	7/14/94

REVISION	R0			
CONTROL DATE:				

COPY NO.: _____ HAS BEEN ISSUED TO HOLDER ON _____

TVA 17207 (OPM-8-83)

1.0 PURPOSE

This procedure describes the method for calculating method detection limits.

2.0 SCOPE

This procedure applies only to work done for the Hot Gas Decontamination Project.

3.0 SUMMARY

At least seven replicate samples are taken through the entire analytical process. The standard deviation is calculated and multiplied by the appropriate t-factor.

4.0 REFERENCES

Title 40, Code of Federal Regulations, Part 136, Appendix B, "Definition and Procedure for the Determination of the Method Deteciton Limit " - Revision 1.1.

5.0 RESPONSIBILITIES

5.1 It is the responsibility of the analyst to perform measurements and calculations in accordance with this procedure, to review results, and to report anomalous results to the supervisor.

5.2 It is the repsponsibility of the supervisor to ensure work is performed in accordance with this procedure and to review results.

6.0 PROCEDURE/REQUIREMENTS

6.1 Prerequisites

Equipment shall have been set up and configured in accordance with the appropriate analytical procedure.

6.2 Limitations and Actions

None

6.3 Requirements

6.3.1 Apparatus/Equipment

See the appropriate analytical procedure.

6.3.2 Reagents and Standards

See the appropriate analytical procedure.

6.4 Calibration

See the appropriate analytical procedure.

6.5 Procedure Instructions

Perform the method detection measurements and calculations in accordance with Attachment 10.1

6.6 Calculating and Reporting Data

Perform calculations in accordance with Attachment 10.1

7.0 QUALITY ASSURANCE PROVISIONS

7.1 Responsibility of Inspection

The analyst and supervisor shall inspect data for consistency and reasonableness.

7.2 Acceptance Criteria

The concentration of analyte should be between one and five times the method detection limit.

7.3 Material Monitoring

None

7.4 Eqiupment Monitoring

None

7.5 Certification

This procedure is certified by the review and approval process.

7.6 Quality Control Sample Requirements

None

8.0 SAFETY

See the appropriate analytical procedure.

9.0 NOTES

None

10.0 ATTACHMENTS AND APPENDICES

10.1 - 40 CFR 136 Appendix B.

APPENDIX B TO PART 136—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT—REVISION 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each

10.1 - Continued

through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\frac{\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2}{n}\right] \qquad S = (S^2)^{\frac{1}{2}}$$

where:

X_i; i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha\,=\,0.99)} \quad (S)$$

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha\,=\,0.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

If $S^2_A/S^2_B>3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681\ (S_{pooled})$$

where 2.681 is equal to $t_{(12,\ 1-\alpha\,=\,0.99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from precentiles of the chi squared over degrees of freedom distribution.

LCL=0.72 MDL

UCL=1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,\ 0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

END OF PROCEDURE